THE ADSORPTION OF VINYL CHLORIDE AND VINYLIDENE CHLORIDE MONOMERS ON THEIR POLYMERS

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by

RALPH GEORGE TORRINGTON, B.Sc. Hons. (Cape Town).

Department of Chemistry,
University of Cape Town,
Rondebosch, Cape,
South Africa.

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S U M M A R Y.

Following semi-quantitative investigations of the kinetics and equilibria of:-

(a) Vinyl chloride monomer vapour adsorbed on polyvinyl chloride;

(b) Vinylidene chloride monomer vapour adsorbed on polyvinyl chloride;

(c) Vinylidene chloride monomer vapour adsorbed on polyvinylidene chloride;

it became evident that, for a number of reasons detailed in the text, it would be worth while to study system (a) in detail. Thorough investigations were therefore made at the two temperatures, 25°C and 42.6°C, and in the pressure range 20 torr to 600 torr, with the following results:

(i) Attainment of equilibrium, especially at the higher pressures, was very slow and as a result only approximate isotherms could be obtained. These isotherms were shown to exhibit hysteresis. Comparison of the amount of monomer adsorbed at the higher pressures, within the above limits, with the amount of krypton required to cover the surface with a monolayer, indicated that multimolecular adsorption occurred. The ascending branches of the isotherms appeared to obey the Freundlich isotherm and the approximate isosteric heats of adsorption calculated from the equilibrium data fell off linearly as the logarithm of the amount of monomer adsorbed increased; as would be expected if the Freundlich isotherm were obeyed. The values of the heats of adsorption found were such that comparison between them and the latent heat of vapourisation of the monomer made it difficult to decide whether the first layer on the surface was chemisorbed or physically adsorbed.

(ii) The kinetic data showed that there was always an initial instantaneous adsorption which was reversible towards pressure,

followed by a very much slower uptake of monomer.

The kinetics of the slow uptake of monomer was studied, at the two temperatures, under both constant pressure and constant volume conditions and was shown to consist of two processes. Initially, at constant pressure, the following equation was obeyed:

$$\frac{ds}{dt} = \frac{k}{p^m}(s_\infty - s)^2$$

where k and m ($m < 1$) are constants at constant temperature and s_∞ is the equilibrium amount adsorbed by this process at pressure p. At a later stage in the reaction a second slow process of the Elovich type started, while the first process continued.

Because of the similarity of the observed equations, to those found for the kinetics for oxygen adsorbed on cuprous oxide, a comparison was drawn between the two systems. The mechanism which had been put forward to explain the kinetics of the latter system could not be postulated for the vinyl chloride system because polyvinyl chloride is covalent whereas cuprous oxide is ionic. That different mechanisms were operating in the two systems, was clearly illustrated when the two systems were compared. In this comparison it was shown that the pressure dependence of the parameters in the rate equation for the two systems were significantly different.

The fact that different mechanisms can lead to the same form of rate equation, is in keeping with the hypothesis that, no unique mechanism can be put forward for Elovich type kinetics and that before a mechanism can be assigned to a reaction which obeys a semi-logarithmic law, it is necessary for the variation of the parameters of the equation with the experimental conditions to be known.

The first slow process in the vinyl chloride system was explained

in terms of a mechanism involving the rearrangement, on the surface, of the monomer molecules adsorbed in the initial rapid process. The second slow process was assigned to a mechanism involving adsorption swelling of the adsorbent.

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C H A P T E R 1.

INTRODUCTION.

1.1 Autoacceleration in free radical polymerisations.

During the course of the free radical polymerisation of many vinyl monomers, such as methyl methacrylate, styrene and vinyl acetate, initiated by substances such as benzoyl peroxide, periods of acceleration in the rate of polymerisation have been observed to occur.[1] This autoacceleration has been found in systems in which the monomer was a solvent for the polymer or in which the polymerising mixture was a concentrated solution of monomers in some solvent in which the polymer was also soluble. In these systems the period of autoacceleration commenced some time after the start of the polymerisation. Simultaneously with the start of the period of acceleration, there is a sharp increase in the average molecular mass of the polymer.

Thus in the polymerisation of methyl methacrylate,[1], it has been shown that for all monomer concentrations up to 40 percent in benzene, the curves showing the extent of reaction plotted against time were roughly independent of the initial concentration, as is required for a first order process. At higher initial monomer concentrations a marked acceleration in rate was observed to occur at an advanced stage of the polymerisation. The stage at which this acceleration in rate occured in each case corresponded to an extent of polymerisation of about 25 percent.

Norrish and Smith[2] concluded, that this period of autoacceleration in the rate of polymerisation and the simultaneous increase in the average molecular mass of the polymer, could only be explained by the assumption that there is a decrease in the rate of termination of the kinetic chain mechanism. This decrease in the rate of termination can be explained by the increased viscosity of the polymerising mixture when the period of acceleration commences.

The period of autoacceleration occurs at a late stage in the polymerisation when the mixture has become viscous owing to the large concentration of polymer molecules. Chain termination involving combination of two free radicals is a very fast reaction which occurs at a large fraction of the collisions between radicals. When the growing polymer molecules bearing

free radical end groups are embedded in the highly viscous mixture consisting of a large proportion of polymer molecules, the rate of termination may be controlled by their rate of diffusion. Thus because of the diminished opportunity for interaction between radicals, the rate of termination will decrease. This fall in the rate of termination will lead to an increase in the steady state concentration of free radicals in the system. The propagation process on the other hand should be insensitive to the viscosity of the medium for two reasons. In the first place its rate constant is much lower than that for the termination process, hence maintenance of an equilibrium population of monomer near each radical places a lesser demand on the diffusion processes. Secondly, one of the reactants is a monomer molecule, the movements of which are not seriously impeded by the long polymer chains in the mixture. The increased steady state concentration of free radicals resulting from the decreased rate of termination therefore results in an increased rate of polymerisation and an increase in the average molecular mass of the polymer.

1.1.1 Autoacceleration in the free radical polymerisation of vinyl chloride and vinylidene chloride.

A period of autoacceleration is also observed when pure vinyl chloride or vinylidene chloride is polymerised in the absence of a solvent for the polymer. Vinyl chloride and vinylidene chloride monomers are not solvents for their polymers and during the polymerisation of the pure monomers solid polymer precipitates from the reaction mixture. The autoacceleration which occurs when these monomers are polymerised differs from that observed when systems such as methyl methacrylate polymerise in two important respects.

Firstly, the autoacceleration in the vinyl chloride and vinylidene chloride systems occurs from the commencement of the polymerisation reaction and secondly, the molecular mass of the polymer formed remains constant.[3,4]

In a series of experiments on the vinyl chloride and vinylidene chloride systems Bengough and Norrish[3,4] were able to show that:

(i) The autoacceleration was not due to the presence of impurities in the manomers.

(ii) "Dead" polymer added to the monomer in the presence of initiator caused an acceleration in the rate.

(iii) "Dead" polymer added to the monomers in the absence of initiator did not cause polymerisation to occur.

(iv) The autoacceleration did not occur when a solvent for the polymer was present in the reaction mixture.

(v) The autoacceleration effect of "dead" polymer measured by the increase of reaction rate was proportional to the amount of polymer present raised to the power of $\frac{2}{3}$.

(vi) The molecular mass of the polymer remained constant.

Bengough and Norrish put forward the hypothesis that the observed autoacceleration in the vinyl chloride and vinylidene chloride systems was due to chain transfer between free radicals in the system and dead polymer. This would give rise to immobile surface radicals which could then grow by addition of monomer. The surface radicals were terminated by chain transfer with a monomer molecule giving "dead" polymer and a new mobile radical. They put forward the following mechanism for the polymerisation:

Initiation	$B \rightarrow 2R$	k_i
Propagation	$R + M \rightarrow R$	k_p
Chain transfer with monomer	$R + M \rightarrow P + R$	k_{tr}
Termination	$R + R \rightarrow P$	k_t
Activation of polymer surface by transfer	$R + P \rightarrow P^* + P$	k_a
Propagation on polymer surface	$P^* + M \rightarrow P^*$	k_p
Termination of surface radical by transfer	$P^* + M \rightarrow P + R$	k_{tr}

In the above mechanism B, R, M, P and P* refer to initiator, mobile free radicals, monomer, dead polymer and polymer conglomerate radicals respectively. k_i, k_p etc. are the velocity constants for the reaction steps. For simplicity all the mobile radicals are treated as having the same reactivity.

Application of steady state conditions to the two types of free radical and making the assumption that the surface area of the polymer is proportional to the amount of polymer raised to the power of two thirds, led to the following expression for the rate of polymerisation.

$$-\frac{dM}{dt} = K(M + K'P^{\frac{2}{3}})(\frac{B}{M})^{\frac{1}{2}}$$ where K and K' are constants.

Extents of polymerisation calculated from the integrated form of this equation fitted experimentally determined curves very well indeed.

The Bengough and Norrish mechanism for the polymerisation of vinyl and vinylidene chloride involves the polymer surface and if this is so, adsorption of the monomer on the surface could play an important role. Therefore, a study of this adsorption could be of interest.

1.2. Adsorption of gases and vapours on solids.

One of the most studied phenomena in physical chemistry is that of adsorption, not only because of the important role which it plays in heterogenious catalysis but also for its own sake.

Adsorption occurs because the free energy at the interface between two immiscible phases tends to a minimum and any process which will reduce the free interfacial energy, will be a thermodynamically favourable one.

At the interface between a solid and a gas, the atoms of the solid at the surface are subjected to unbalanced forces perpendicular to the surface and therefore possess a certain degree of unsaturation. This unsaturation can be reduced and the free energy of the surface lowered by the adsorption of gas molecules on to the surface of the solid.

As adsorption always occurs with a reduction in free energy and as there is usually a reduction in the entropy of the system, due to adsorbed

gas molecules losing certain degrees of freedom when confined to the surface, application of the thermodynamic relationship

$$\Delta G = \Delta H - T\Delta S$$

shows that ΔH must be negative, i.e. adsorption will be an exothermic process.

The main work of saturating a surface is usually accomplished by condensation of a single layer of molecules and in such cases the adsorption is termed unimolecular or monomolecular. However, adsorptions involving the condensation of several layers are by no means infrequent and these are called multimolecular.

1.2.1 Physical adsorption and chemisorption.[5]

Although the degree of unsaturation of surfaces can vary widely, experience has taught that there are only two kinds of adsorption. If the valency requirements of the atoms of the solid are satisfied by bonding to adjacent atoms, and if no electron transfer or sharing can occur between adsorbate molecules and atoms of the adsorbent then the only forces available for holding gas molecules on to the surface are those of physical attraction such as exist between molecules in a liquid. This kind of adsorption in which the adsorbate molecules are held on to the absorbent surface by van der Waals' type forces is known as van der Waals' adsorption or as physical adsorption. On the other hand, if the valency requirements of the surface atoms are not fully satisfied by bonding to other atoms of the solid then adsorption can result by electron transfer between the surface atoms and the adsorbate molecules. In such cases the forces holding the adsorbate molecules on to the surface are similar to those forces found in chemical bonding. This type of adsorption is known as chemisorption.

There are five criteria which can be used to distinguish between the two types of adsorption:

(i) The magnitude of the heat of adsorption.

(ii) The temperature range over which adsorption occurs.

(iii) The rate at which the adsorption proceeds.

(iv) The number of layers of adsorbate on the surface.

(v) Specificity.

As the forces involved in physical adsorption are those of physical attraction, it follows that the differential heat of physical adsorption should be of the order of the latent heat of condensation of the adsorbate. Because of this parallelism between physical adsorption and liquification of the adsorbate, physical adsorption should only occur at temperatures below the critical temperature of the adsorbate. Furthermore, physical adsorption should be non-activated and occur instantaneously, just as no activation energy is required for the liquification of a gas. Physical forces of attraction exist between all molecules, hence physical adsorption should occur on all surfaces provided the temperature and pressure conditions are suitable and it should be possible for multimolecular adsorption to occur.

For chemisorption on the other hand, the forces involved are similar to those found in chemical bonding and therefore the differential heat of chemisorption will be of the order of that found for chemical bonds. As heats of chemical reaction are generally very much larger than heats of liquification, it is to be expected that heats of chemisorption will usually be very much larger than heats of physical adsorption. Chemisorption can occur at temperatures well above the critical temperature of the adsorbate and because of its similarity to chemical reactions might well be activated, occurring only at a measurable rate at elevated temperatures. Chemisorption will be specific and will only occur on some surfaces and not on others. Also the surface must be clean and free of contaminants. Because chemisorption involves electron transfer between the adsorbate and the adsorbent it will cease when the adsorbate can no longer make contact with the surface.

Hence chemisorption stops once a monomolecular layer of adsorbate has been chemisorbed on to the surface.

None of the above criteria for distinguishing between the two kinds of adsorption are infallible in all cases. Weak chemisorption can occur in the van der Waals' adsorption temperature range and heats of chemisorption can fall to fairly low values comparable to physical adsorption, particularly at high surface coverages.[6] Distinction between physical and chemisorption on grounds of velocity is liable to be blurred for two reasons. First, many surfaces are so unsaturated that they undergo rapid chemisorption even at low temperatures.[7] Second, if an adsorbent is porous, penetration of adsorbate to the interior may be an extremely slow process. This penetration may result in chemisorption at interior surfaces, but it may also be physical adsorption or even solution of the gas.

1.2.2 Measurements in the field of adsorption.

Early workers in the field used powder surfaces, often of doubtful cleanliness. Their investigations were mainly aimed at obtaining adsorption isotherms, adsorption isobars and heats of adsorption.

Adsorption isotherms and isobars were obtained using volumetric methods. Heats of adsorption were determined from the isotherms, the isosteric heat of adsorption, or by using calorimetric methods. The calorimeters used, and still used to-day, fall into two classes:

(i) Isothermal calorimeters.

(ii) Adiabatic calorimeters.

The isothermal calorimeters were modifications of the Bunsen ice calorimeter in which the heat evolved during the reaction caused a phase change in a surrounding liquid or solid such as liquid air,[8] diphenyl ether,[9] phenol[10] and others.

In the adiabatic calorimeter[11,-13] the heat evolved caused a measurable temperature rise in the adsorbent. Precautions were taken to ensure that heat loss to the surroundings was minimised and that the heat

evolved caused a uniform temperature rise throughout the adsorbent.

Because of the doubtful nature of the state of the surface these early results were often irreproducible and hence difficult to interpret. Later workers used filaments,[7] evaporated films[14] and powders, which had been subjected to rigorous cleaning procedures, as adsorbents. This has led to better reproducibility.

Modern methods for studying the adsorbed layer include: measurement of changes in work function,[15] infrared measurements,[16] magnetic susceptibility measurements[17 - 20] and electron diffraction methods.[21]

1.2.3 Heats of Adsorption.

The magnitude of the heat of adsorption is the most single characteristic property of an adsorption and determination of reliable heats is therefore of considerable importance.

1.2.3.1 The isosteric heat of adsorption.

When the Clausius-Clapyron equation is applied to a set of thermodynamically reversible isotherms, isosteric heats of adsorption are obtained. These are defined by the equation:

$$q_{isosteric} = +\mathcal{R}T^2\left(\frac{\partial \ln p}{\partial T}\right)_\theta$$

where $q_{isosteric}$ is the isosteric heat of adsorption, T is the absolute temperature, p is the equilibrium pressure of adsorbate at a surface coverage θ, and $\mathcal{R}$ is the gas constant.

The isosteric heat of adsorption can be obtained from a set of isotherms by plotting the logarithm of the equilibrium pressure against the reciprocal of the absolute temperature for a constant amount adsorbed. Provided that the temperature range is not too wide and that the adsorbate can be treated as an ideal gas, the plot should be linear and from the slope of the plot $q_{isosteric}$ can be calculated using the relationship.

$$q_{isosteric} = +\ 2.303\ \mathcal{R} \times \text{slope}.$$

1.2.3.2 The differential heat of adsorption.

If heats are measured isothermally at particular values of θ in such a manner that no work is done during the adsorption, the true differential heat q_{diff} is obtained. It is possible to show thermodynamically that

$$q_{diff} = +RT^2\left(\frac{\partial \ln p}{\partial T}\right)_\theta - RT$$

so that

$$q_{isosteric} = q_{diff} + RT$$

1.2.3.3 Calorimetric heats of adsorption.

When small quantities of gas are admitted to a surface and adsorbed, the heat evolved and measured calorimetrically would be equal to q_{diff} if none of the work done during the adsorption were transferred to the calorimeter as heat. On the other hand, if all the work done were transferred to the calorimeter as heat, the heat liberated would be equal to $q_{isosteric}$. In practice the calorimetric differential heat is intermediate between the true differential heat and the isosteric heat.

1.2.3.4 Reproducibility of measured heats of adsorption.

Measurements by different investigators of the heat of physical adsorption of a given gas on a given surface usually agree within experimental error. With chemisorption, however, this is not the case.

Differences have been found between powdered samples of the same absorbent,[22, 23] whereas on evaporated films heats are usually reproducible[24, 25] and higher than those found on powdered samples of the same absorbent. Occasionally, as in the case of hydrogen and carbon monoxide adsorbed on copper,[24, 26, 27] the heat of adsorption obtained from a film is lower than that obtained from a powder. These differences can be explained in terms of contamination of the powder. In most cases the contaminent reduces the adsorptive capacity of the system, but occasionally the impurity might have a higher adsorptive capacity than the pure adsorbent and this will result in enhanced values of the heat of adsorption.

Heats of chemisorption may vary with the physical form of a clean adsorbent. Thus whereas the heat of adsorption of hydrogen on a tungsten film is 45 k cal/mole,[24, 25] on a tungsten filament it has been found to be 29 k cal/mole.[28]

A phenomenon which is often observed is that the initial heat of adsorption changes with temperature; being higher at the higher temperature.[24, 29, 30] It is also usually observed in these cases that the rate of adsorption is rapid at the lower temperature and slower at the higher temperature. This can be explained by postulating that different mechanisms for the adsorption operate over different temperature ranges. Thus at the lower temperature a weak chemisorption with low activation energy may operate whereas at the higher temperature a stronger chemisorption with a higher activation energy operates.

Pretreatment of the adsorbent can also influence the heat of chemisorption. This is most noticeable with oxide adsorbents in which different methods of pretreatment have been found to alter the structure and the stoichiometric formula.[31]

1.2.3.5 Variation of the heat of adsorption with surface coverage.

The general trend observed for the variation of the heat of chemisorption with surface coverage is that the heat decreases as the surface becomes covered. The way in which the heat changes with coverage varies both with the adsorbate and with the adsorbent. Thus the heat of adsorption of nitrogen on tungsten filaments and ribbons[32] remains constant as the surface coverage increases. The heat of adsorption of hydrogen on tungsten powder[33] decreases logarithmically with coverage. The heat of adsorption of hydrogen on iron films[34] decreases linearly with surface coverage. For other systems more complex changes of heat of adsorption with coverage have been observed.[35]

Three main explanations have been advanced to account for the generally observed trend of decreasing heat of adsorption with increasing

surface coverage. The first of these theories, initially due to Constable[36] and Taylor,[37] is the theory of surface heterogeneity. It is postulated that there are sites of different energies on the surface. The more active sites will be covered first and the ones of lower activity last. Hence as adsorption proceeds there is a decrease in activity of the surface and hence a fall in the heat of adsorption.

There is some qualitative evidence for this theory. The value of the work function has been found to be different on different crystal faces[38] and Beeck and co-workers[39, 40] have shown that different crystal faces have different catalytic activity. Also very small amounts of a poison, insufficient to cover the whole surface, can effectively inhibit a catalytic reaction, indicating that only a few sites on the surface are active. The existence of different bonding states on the surface has been shown by Ehrlich[41] and Redhead[42] in their investigation of the manner in which carbon monoxide is desorbed from a tungsten filament.

The second explanation, due to Roberts,[7] is that the decrease of heat of adsorption with coverage occurs because the adsorbed molecules on the surface repel each other. Testing of this theory by calculating the repulsions between the molecules on the surface on the basis of overlapping electron clouds and dipole-dipole interaction is difficult because of the lack of quantitative data. In the few cases where calculations have been performed, the agreement between calculated and observed values of the heat of adsorption have not been good. Usually the drop in heat observed is greater than that calculated. Also a theory based on repulsion between molecules will not explain a logarithmic fall of heat of adsorption with coverage because this would imply the greater repulsion occurring when the molecules are most widely separated on a sparsely covered surface.

The third explanation is due to Eley[43] and Schwab[44] in which they ascribe heat falls to the filling of different electron energy levels in the solid. This theory may be applicable[45] in certain chemisorptions

on oxides, where the adsorption involves a limited number of orbitals, arising from the small number of defects or impurities associated with non-stoichoimetry.

1.2.4 Adsorption isotherms.

Brunauer *et al*[46] have suggested that experimental isotherms can be classified as belonging to one or other of the five type shown in Figure A. Over the last fifty years thousands of isotherms have been reported and most of them do fit into this classification.

Type I isotherms are the kind found in chemisorption, where a monolayer forms on the surface of the adsorbent. Once the monolayer forms no further adsorption occurs, i.e., the isotherm has a saturation limit. The other four types are associated with multimolecular adsorption and porous type adsorbents.

1.2.4.1 Monolayer adsorption.

Three of the empirical relationships which give Type I isotherms have been given theoretical significance.

(i) The Langmuir isotherm which has the empirical form $\frac{p}{s} = c + c'p$ where c and c' are constants, p = equilibrium pressure and s = amount adsorbed.

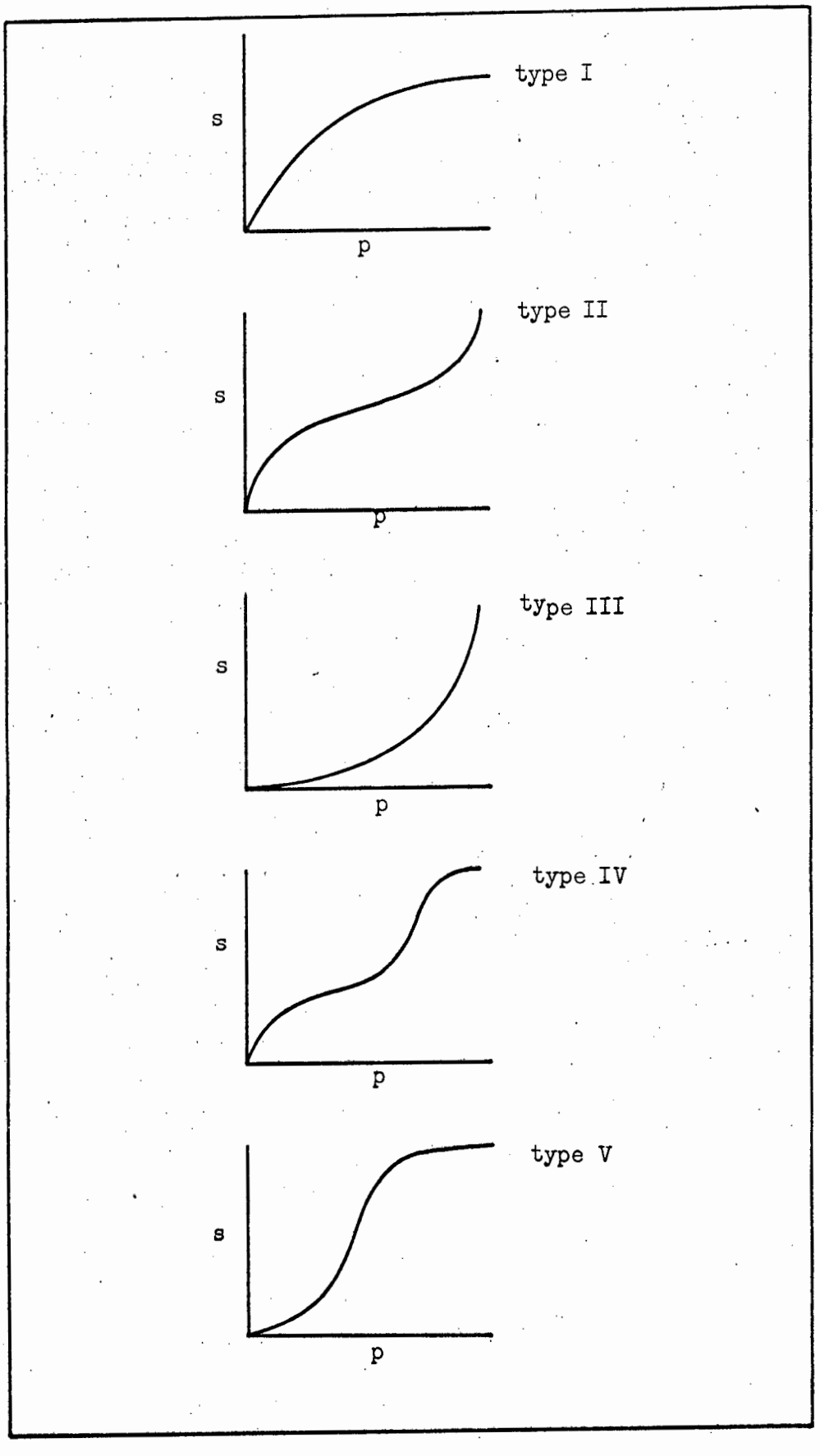
(ii) The Freundlich isotherm which is of the form $s = cp^{\frac{1}{n}}$ where c and n are constants and $n > 1$.

(iii) The Temkin isotherm which is obeyed in the range 20 to 80 percent of the adsorption and has the form $s = c + c' \log p$ where c and c' are constants.

In deriving theoretical isotherms three approaches are possible. First, in kinetic terms, the condition for equilibrium is that the velocities of adsorption and desorption are equal and isotherms may be obtained by equating these velocities. Second, in statistical terms, the equilibrium constant is given by a ratio of partition functions of vacant sites, adsorbed

FIG. A

THE FIVE BASIC ISOTHERM SHAPES



molecules and gas phase molecules, and isotherms may be obtained by equating this ratio to the corresponding ratio of concentration. Third, equilibrium may be approached thermodynamically, either using the condition that the change in free energy on transferring an infinitesimal amount of gas from the gas phase to the surface at constant temperature is zero, or alternatively using the Gibbs adsorption equation.

In the theoretical derivation of the Langmuir isotherm [47, 48] the following assumptions are made:

(i) Adsorption is localized and takes place only through collision of gas molecules with vacant sites.

(ii) Each site can accommodate only one adsorbed particle.

(iii) The energy of an adsorbed particle is the same at any site on the surface and is independent of the presence or absence of nearby adsorbed molecules. This implies that the heat of adsorption does not alter with surface coverage.

In the theoretical derivation of the Freundlich isotherm the main assumption is that there is a logarithmic fall of heat of adsorption with surface coverage,[49, 50] this fall in the heat of adsorption being due to surface heterogeneity and not molecular repulsions.

The Temkin isotherm can be derived[51] by assuming a linear decrease of heat of adsorption with surface coverage. The linear decrease in the heat of adsorption with surface coverage can arise due to either surface heterogeneity or to replusion between molecules on the surface.

Trapnell[52] has pointed out that when testing the fit of a set of experimental points to one of the above isotherms three conditions must be satisfied.

(i) The data must give the correct plot.

(ii) The q - s curves must obey the form implied by the isotherm in question.

(iii) The experimental data must cover the appropriate range of the amount adsorbed. In testing obedience to the Langmuir and Freundlich isotherms the data must apply to the widest range of coverage; in testing the Temkin isotherm the coverage must lie between 20 and 80 percent.

1.2.4.2 Multimolecular adsorption.

The generalisation of the Langmuir mechanism to cover the other four types of isotherm was introduced by Brunauer, Emmett and Teller.(53) This theory not only puts forward a simple procedure for the determination of the monolayer capacity, but it claims to be able to reproduce with the same set of parameters the course of the isotherms at different temperatures and also to calculate the heat of adsorption from a single isotherm.

The theory retains the concept of fixed adsorption sites but allows for the formation of an adsorbed layer more than one molecule thick; the state of dynamic equilibrium which Langmuir postulates for the monolayer is assumed to hold for each successive molecular layer and it is then possible, with the aid of certain simplifying assumptions, to arrive at an equation for the adsorption isotherm. The simplifying assumptions used are:

(i) A fraction of the surface θ_o is assumed to be bare. A fraction of the surface θ_1 is assumed to be covered with a monolayer.
A fraction of the surface θ_2 is assumed to be covered with a layer two molecules thick.
A fraction of the surface θ_n is assumed to be covered with a layer n molecules thick.

(ii) The heat of adsorption in the monolayer is E_1, the heat of adsorption in all other layers is equal to L the molar heat of condensation of the adsorbate.

(iii) When the pressure reaches the saturation vapour pressure p^o then the vapour condenses on the adsorbent as a bulk liquid, i.e., at $p = p^o$ the number of adsorbed layers is infinite.

(iv) The frequency of vibration of oscillations of the molecules perpendicular to the surface is the same for all layers.

Using these assumptions and applying the Langmuir mechanism of dynamic equilibrium to the layers the B.E.T. equation

$$\frac{p}{s(p^o-p)} = \frac{1}{s_m c} + \frac{c-1}{s_m c}\frac{p}{p^o} \qquad \text{----------(A)}$$

can be derived where s_m = volume of adsorbate which will cover the surface with a monolayer, $c = e^{(E_1-L)/RT}$ and p^o = saturated vapour pressure of the adsorbate.

The equation can be tested by plotting $\frac{p}{s(p^o-p)}$ against $\frac{p}{p^o}$. This plot should be linear and s_m and c can be found from the slope and intercept. s_m and E_1 calculated from c and the known value of L can now be compared with independent estimations of these quantities to test the correctness of the theory.

In practice it has been found that the B.E.T. equation does reproduce the course of many Type II isotherms reasonably well over the range $\frac{p}{p^o}$ = 0.05 to $\frac{p}{p^o}$ = 0.30 or sometimes less. The fit can sometimes be extended to higher pressures by using a modified equation which is arrived at by assuming that the total number of layers adsorbed is not infinite but a finite number n. The equation derived in this way is:

$$\frac{s}{s_m} = \frac{c(p/p^o)}{1 - p/p^o} \cdot \frac{1 - (n+1)(p/p^o)^n + n(p/p^o)^{n+1}}{1 + (c-1)(p/p^o) - c(p/p^o)^{n+1}} \qquad \text{------(B)}$$

The general shape of the rather rare Type III isotherm is reproduced by equation A with values of c less than 2 but quantitative agreement is rather poor.[54] To reproduce isotherms of Type IV and V it is necessary to use a somewhat complicated modification of equation B which contains a fourth deposable constant. This gave moderate agreement with the adsorption branch of the isotherm in the one case in which it was tried.[54]

The B.E.T. theory has been criticised[54] on the grounds that it does not take into account variation of E_1 from one region of the surface to

another and that this might account for its failure at relative pressures below 0.05. A second criticism is that in the absence of horizontal neighbours in the higher layers, the adsorbed molecules do not have the full value of the co-ordination number found in the liquid. Hence the heat evolved during adsorption in the these layers will not be the latent heat of condensation but only a fraction of it.

1.2.4.3 Hysteresis.

Adsorption isotherms are not always reversible, i.e., the path traced out when measuring the amount adsorbed with increasing pressure is different to that traced out when the pressure is reduced. This phenomenon is known as hysteresis and has been observed to occur with all five types of isotherm. In some systems the cycle is reproducible, in others it is not.[55]

In some cases at least hysteresis is associated with a very slow approach to equilibrium, an approach which may take days or even weeks for its attainment. In other cases, although a number of suggestions such as capillary condensation, differences between the mechanisms of adsorption and desorption and the opening to adsorption of previously closed areas by adsorption swelling, have been putforward, no generally accepted explanation has yet been advanced.

1.2.5 Kinetics of adsorption.

Evidence for activated adsorption on powders has been of two kinds.

(i) Many solids adsorb the same gas in different ways at different temperatures. Thus Dewar[8] found the heat of adsorption of oxygen on charcoal tc be 4 k cal/mole at liquid air temperature whereas other investigators[12,56] found a value of 80 k cal/mole at 0°C.

(ii) Adsorption isobars determined for many powders and foils[47,57,58,59] show maxima and minima. If only one kind of adsorption occurs then the amount adsorbed at constant pressure should continuously decrease with increasing temperature. The observed maxima and minima can be explained in terms of different processes occurring over different temperature ranges. Thus it has been suggested[47,60] that the process in the low temperature region with low heat of adsorption was physical adsorption whereas the process, or processes, occurring in the higher temperature range was chemisorption.

Taylor[60] has pointed out that as chemisorption seems to proceed to a measurable extent only above certain minimum temperatures, it must involve an appreciable activation energy.

The theory of activated adsorption has been criticised on three grounds:

(i) The slow process could be diffusion or solution. Thus Ward[61] found that for hydrogen adsorbed on copper at $0^{\circ}C$ there was a rapid initial adsorption followed by a slow uptake. The heat of adsorption for the rapid adsorption was 10 k cal/mole indicating chemisorption. The extent of the slow uptake was found initially to be proportional to the square root of time and this Ward showed to be characteristic of a diffusion or solution process when the concentration of adsorbate at the centre of the solid particle is effectively zero.

(ii) The surface of the adsorbent could be contaminated as powders are difficult to clean. Thus on clean tungsten filaments and nickel films hydrogen chemisorption is rapid and apparently non-activated, whereas on an oxygenated surface there is a slow uptake of hydrogen.[7,39]

(iii) In the low temperature range where adsorption was thought to be wholly physical, chemisorption is now known to occur. Thus for hydrogen adsorbed on Cr_2O_3[29] at liquid air temperature the heat of adsorption is too large for physical adsorption and the oxide has been found to be active as a catalyst in the hydrogen-deuterium exchange reaction at -195°C.

Of the three criticisms, (ii) is the most difficult to refute. The theory of activated chemisorption does not exclude non-activated chemisorption which could occur at low temperatures on a surface with a high degree of unsaturation, i.e., it is possible for non-activated chemisorption to occur in the physical adsorption temperature range.

In the case of the first criticism, that the slow uptake may be absorption; this may be justified in some cases with powders and bulk adsorbents possessing pores and capillaries but it seems less likely on filaments and films which have large surface area to volume ratios.

As far as criticism (ii) is concerned, it is probably impossible to prove that a surface is absolutely clean. However, experiments performed using evaporated films, prepared taking elaborate precautions against contamination, have shown slow uptake of adsorbate to occur. Thus Rideal and Trapnell[14] reported a slow adsorption of oxygen on tungsten film after the occurrence of an instantaneous process. Porter and Tomkins[34] found a similar effect occurs during the adsorption of hydrogen and carbon monoxide on evaporated iron films. These latter authors also found that reducing the surface area twenty-fold by increasing the presintering temperature from 78K to 638K caused only a 40 percent increase in the ratio of amount of instantaneous adsorption to that of slow adsorption. This, together with other kinetic evidence, led them to deduce that the slow adsorption was a surface effect.

1.2.5.1 The Elovich Equation.

The most commonly found kinetic equation in slow chemisorptions is the Elovich equation or, as it is sometimes called, the Zeldovich-Roginsky equation. The use of this equation to represent rates of adsorption, the variation of its parameters with experimental conditions, observed anomalies and the various adsorption mechanisms which lead to the equation have been comprehensively reviewed by Low.[62]

The equation has the form

$$\frac{ds}{dt} = ae^{-\alpha s} \quad - - - - - - - - - - - - - (1)$$

where s is the amount adsorbed and a and α are constants.

The integrated form of the equation assuming s = 0 when t = 0 is:

$$s = \frac{2.3}{\alpha} \log (t + t_o) - \frac{2.3}{\alpha} \log t_o \quad - - - - (2)$$

where $t_o = \frac{1}{a\alpha}$.

If a volume of gas s_o is adsorbed instantaniously before equation (1) begins to apply then the integrated form of the equation becomes:

$$s = \frac{2.3}{\alpha} \log (t + k) - \frac{2.3}{\alpha} \log t_o \quad - - - - (3)$$

where $k = t_o e^{\alpha s_o}$.

If k is negligible in comparison with t then equation (3) becomes

$$s = \frac{2.3}{\alpha} \log t - \frac{2.3}{\alpha} \log t_o$$

Equation (1) can be tested and the parameters a, α and k evaluated by graphical and numerical methods.[34,63,64,65]

1.2.5.2 Mechanisms leading to the Elovich Equation.

Several divergent adsorption mechanisms have been put forward to account for the Elovich equation. These can be roughly divided into three classes.

In the first of these classes the activation energy of chemisorption is assumed to increase linearly with surface coverage. This

variation of activation energy with surface coverage being due to (a) molecular repulsion between the adsorbed molecules on a uniform surface or to (b) the surface itself being non-uniform.

Brunauer *et al*,[51] using these concepts, derived a form of the Elovich equation for both (a) and (b) above.

The second kind of derivation due to Gundry and Tompkins[66] involves the concept of a precursor state in which the adsorbate is weakly chemisorbed before going over to the final more strongly bound chemisorbed state. As the number of molecules adsorbed in the final state increases the activation energy for the transfer of molecules from the precursor state to the final state increases. A linear increase in this activation energy leads to the Elovich equation. In a sense this model of the adsorption process is similar to the first model, inasmuch that both models postulate a linear increase of activation energy with amount adsorbed, but the Tompkins mechanism does not require a non-uniform surface nor does it have to postulate repulsion between molecules. Also depending on the form of the isotherm for the molecules physically adsorbed which are in equilibrium with the precursor state, the pressure dependence of the initial rate can be accounted for.

The third kind of mechanism initially proposed by Taylor and Thon[65] uses Val'kenshtein's theory. In this theory the very act of adsorption generates adsorption sites. In chemisorption the mechanism consists of a quasi explosive production of active sites upon contact between the adsorbate and the adsorbent. This is offset by a first order spontaneous decay of sites resulting in an initial steady state site concentration . . and is marked at that stage by an amount of gas that is instantaneously adsorbed. From that point on slow adsorption occurs with bimolecular disappearance of sites and the corresponding exponential decrease in the rate of adsorption.

Jennings and Stone[67] have pointed out that mere linearity of the s- log t plots cannot be used as a criterion for the choice of a

mechanism. A knowledge of the effects of change of experimental variables on the kinetics may permit such choice and so is necessary. A comparison of effects is desirable in view of the different mechanisms employed in interpreting the exponential rate law. However, Low[62] has made the observation that such a comparison at present would be of dubious value because of the complexity of experimental results and their occasional contradictory nature. Low[62] concludes by stating that none of the present models appear to be satisfactory. The more general models, such as that of Taylor and Thom, suffer because their flexibility seems to preclude quantitativity, whereas the more quantitative approaches seem to be imbued with too much rigour and cannot account for the complex behaviour found experimentally.

The wide applicability of the Elovich equation to phenomena such as chemisorption on very different adsorbents and also to some oxidations has arroused criticism. Thus Parravono and Boudart[68] found that a number of different processes such as bulk or surface diffusion and activation or deactivation of catalyst surfaces, as well as chemisorption, may be represented by semi-logarithmic formulae, and they make the comment that is appears futile to explain this formulation in terms of a unique mechanism.

1.2.6 Adsorption on polymers.

In recent years a number of papers [69 - 78] on the sorption of gases such as nitrogen, krypton, argon on polymers such as teflon, nylon and polyvinyl chloride have been published.

These studies were done at temperatures near the boiling points of the adsorbates and were mainly concerned with the determination of surface areas and thermodynamic functions calculated from the experimental isotherms.

For most of the systems studied it was reported that the isotherms obtained were reversible with no exhibition of hysteresis. Exceptions to

this were reported in two of the papers referred to above. Graham[73] found that for the sorption of ethane, n-butane and n-octane on a teflon surface, a rapid process initially occurred which was followed by a much slower process. He considered the rapid process to be adsorption and the slower process to be absorption and separated them by extropolating the s - t curves obtained to zero time.

Hoburg and co-workers[76] found for the adsorption of nitrogen and argon on polystyrene that hysteresis occurred when desorption was attempted. These authors found that reversible isotherms, which were suitable for thermodynamic analysis, could be obtained after equilibrating the polymer with argon at a relative pressure of 0.95 at 75 - 77 K for 8 days. They noted that the polymer sorbed argon throughout the whole of this period but that 90% of the total amount was sorbed within 2 days. They attributed the hysteresis to penetration of the gas molecules into the polymer structure. In neither paper was any attempt made to study the kinetics of the slow process.

The general conclusion drawn from these studies[69 - 78] was that the surface of the adsorbents was highly heterogeneous with adsorption occurring in patches or clusters on the surface.

1.3 The objectives of the research.

The Bengough and Norrish mechanism for the polymerisation of vinyl and vinylidene chloride monomers involves the surface of the formed polymer. In this mechanism adsorption of the monomer on the polymer surface could be of importance.

The objective of the research is thus to study the adsorption of gaseous vinyl and vinylidene chloride monomers on their respective polymers in the temperature range over which they are polymerised and to see if any points of similarity exist between them and inorganic systems which have already been studied.

It is intended:

(1) to perform a series of preliminary experiments on the two systems to see if adsorption occurs and if adsorption isotherms can be measured and hence isosteric heats of adsorption obtained;

(2) if possible to measure rates of adsorption and to derive kinetic expressions to fit the observed rates of adsorption.

CHAPTER 2.

EXPERIMENTAL I.

PRELIMINARY STUDY.

2.1 Purification of reagents.

The method employed for the purification of the two monomers has been described by Bengough and Norrish.[3,4] In essence the apparatus for the purification of the two monomers, (Fig. 1), consisted of a washing train followed by a vacuum distillation stage and liquid storage traps. Provision was also made for removing monomer from the system for purposes of calibration, purity checks and polymer preparation. The whole apparatus could be evacuated by means of a mercury vapour pump backed by a rotary oil pump.

Vinyl chloride was obtained from a commercial cylinder and as the main impurity was acetylene, this was removed by passing the monomer vapour through a solution of ammonical copper(I) chloride contained in a wash bottle and then passing the emergent vapour up a glass packed scrubbing column down which trickled the same reagent. The monomer thus freed from acetylene was then passed through water and dilute sulphuric acid to free it from ammonia and then over soda lime, silica gel and phosphorous pentoxide.

The dried vapour was condensed in the boiler of the previously evacuated fractionating column by surrounding the boiler with a dewar vessel containing solid dry ice and filling the cold finger on the top of the column with a slurry of dry ice in acetone. When sufficient monomer had collected in the boiler, the vacuum distillation was performed.

The vapour at the top of the column was removed by means of the grooved stopcock A thus ensuring a slow rate and fine control of the distillation. The vapour drawn from the top of the column was condensed in the storage traps by surrounding them with dewar vessels containing liquid nitrogen. As recommended by Bengough and Norrish, three fractions were taken, the first and last fractions being discarded and the middle one kept for subsequent use.

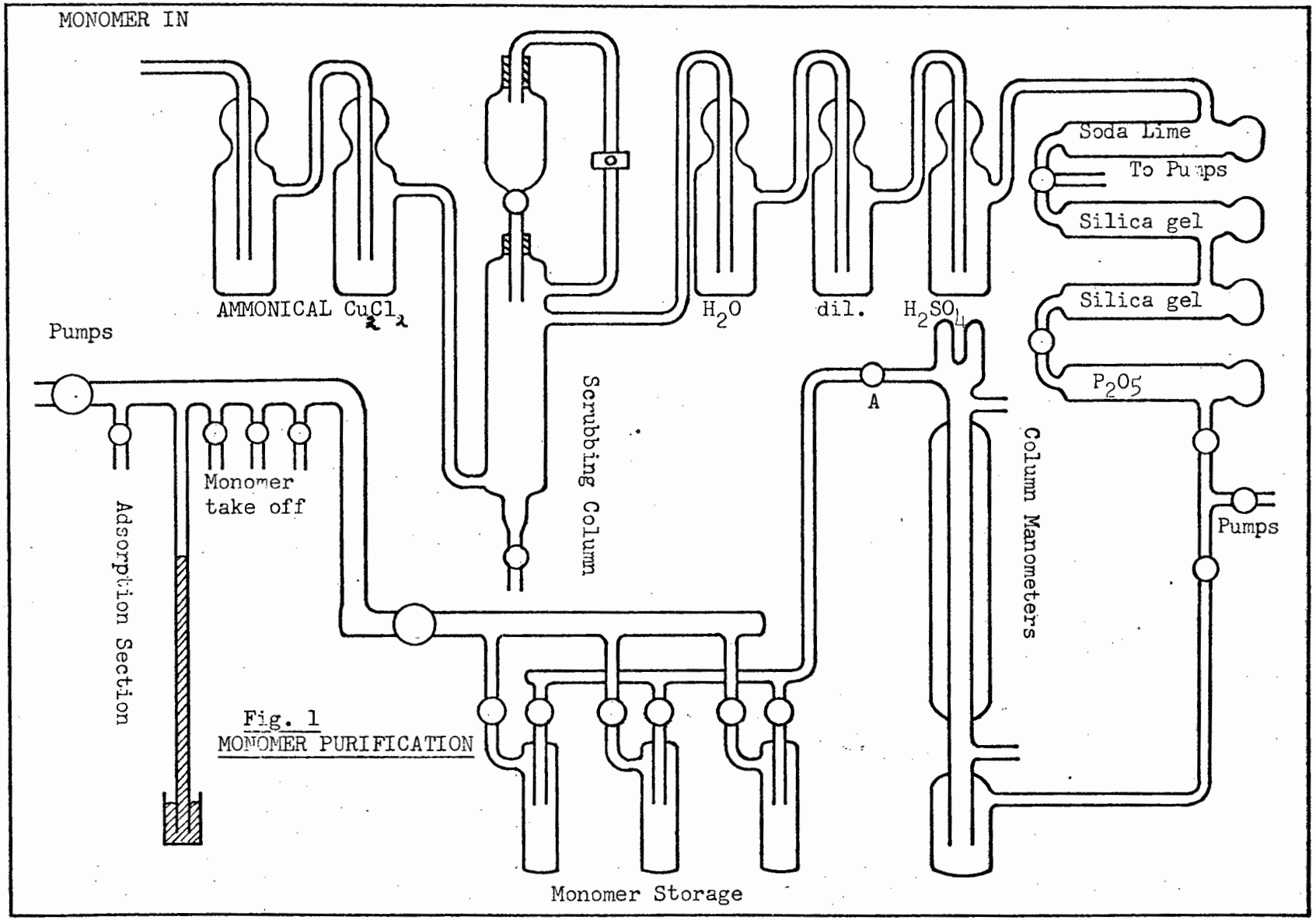


Fig. 1
MONOMER PURIFICATION

Vinylidene chloride was prepared by the action of alcoholic potash on 1,2,2-trichloroethane at 75°C. The purification of this monomer was the same as for vinyl chloride with the exception that the acetylene removal and subsequent ammonia removal steps were not necessary and were therefore omitted.

2.2 Calibration of the apparatus for monomer removal.

To check the purity of the monomers prepared and purified by the above method and to prepare the polymer required for the adsorption experiments, it was necessary to remove known amounts of monomer from the system. The calibration of the system for the removal of these known amounts of monomer was carried out as follows:

Small tubes of about 6 to 8 ml capacity, made with a constriction at which they could be sealed off, were attached to the "monomer take off" points on the apparatus (Fig.1) by means of B10 glass ground joints. The tubes and the apparatus were evacuated for 30 minutes and then the stopcocks connecting the tubes to the apparatus were closed. The take off section was then filled with monomer and the pressure of the monomer in the section and the room temperature recorded.

A sample of monomer was then removed by condensing the monomer into one of the "take off" tubes surrounded by a dewar vessel containing liquid nitrogen. When sufficient monomer had condensed in the tube, the stopcock was closed, the final pressure recorded, the tube sealed off at the constriction and removed from the apparatus. After allowing the tube and contents to come to room temperature, the tube was weighed. After weighing the tube was broken open, care being taken to prevent loss of any slivers of glass. To ensure that all the monomer was removed, the pieces were placed in a vessel attached to the pumps and evacuated for 30 minutes. After evacuation the pieces were reweighed and the mass of

FIG. 2

CALIBRATION CURVES FOR THE REMOVAL OF MONOMER

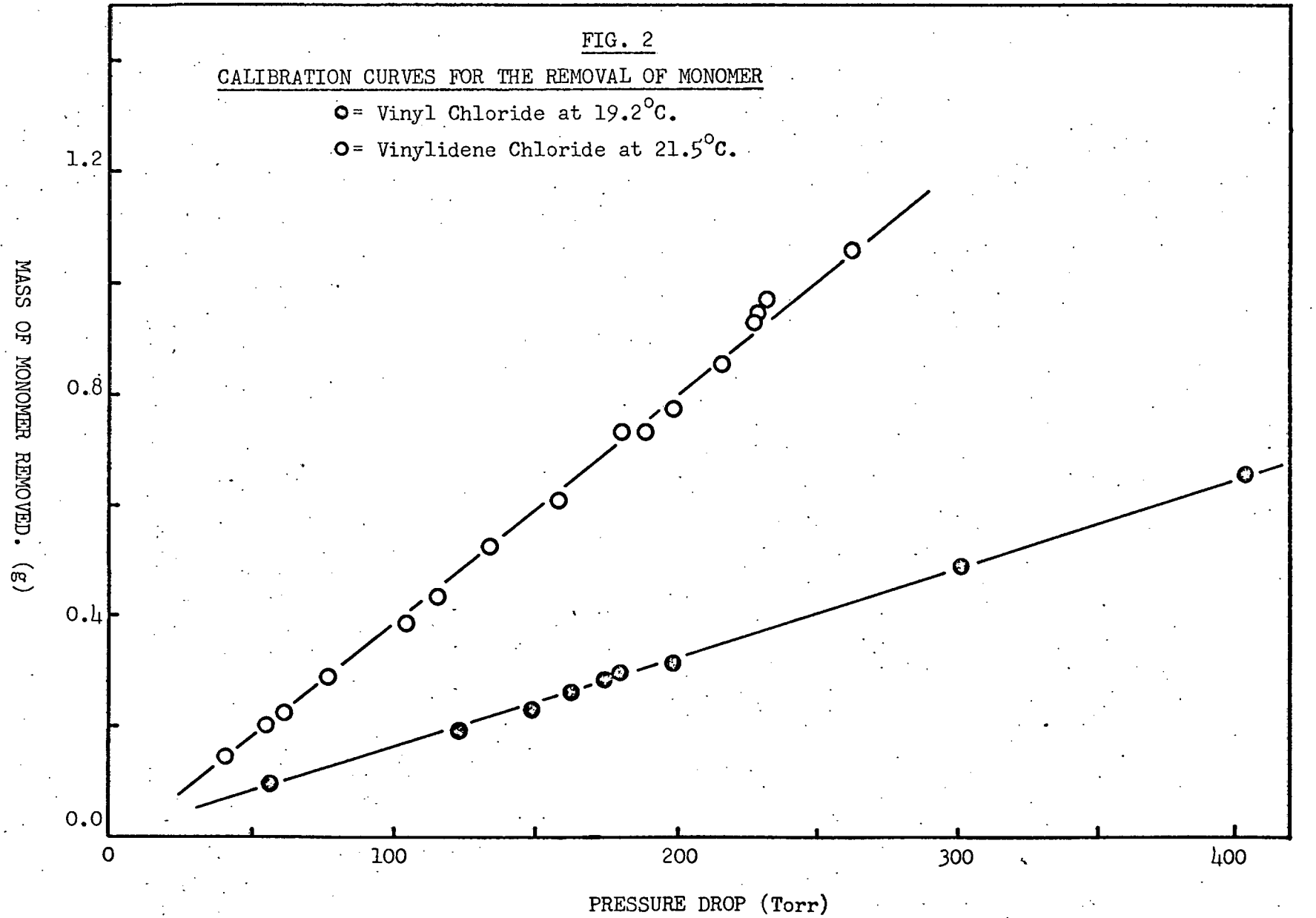
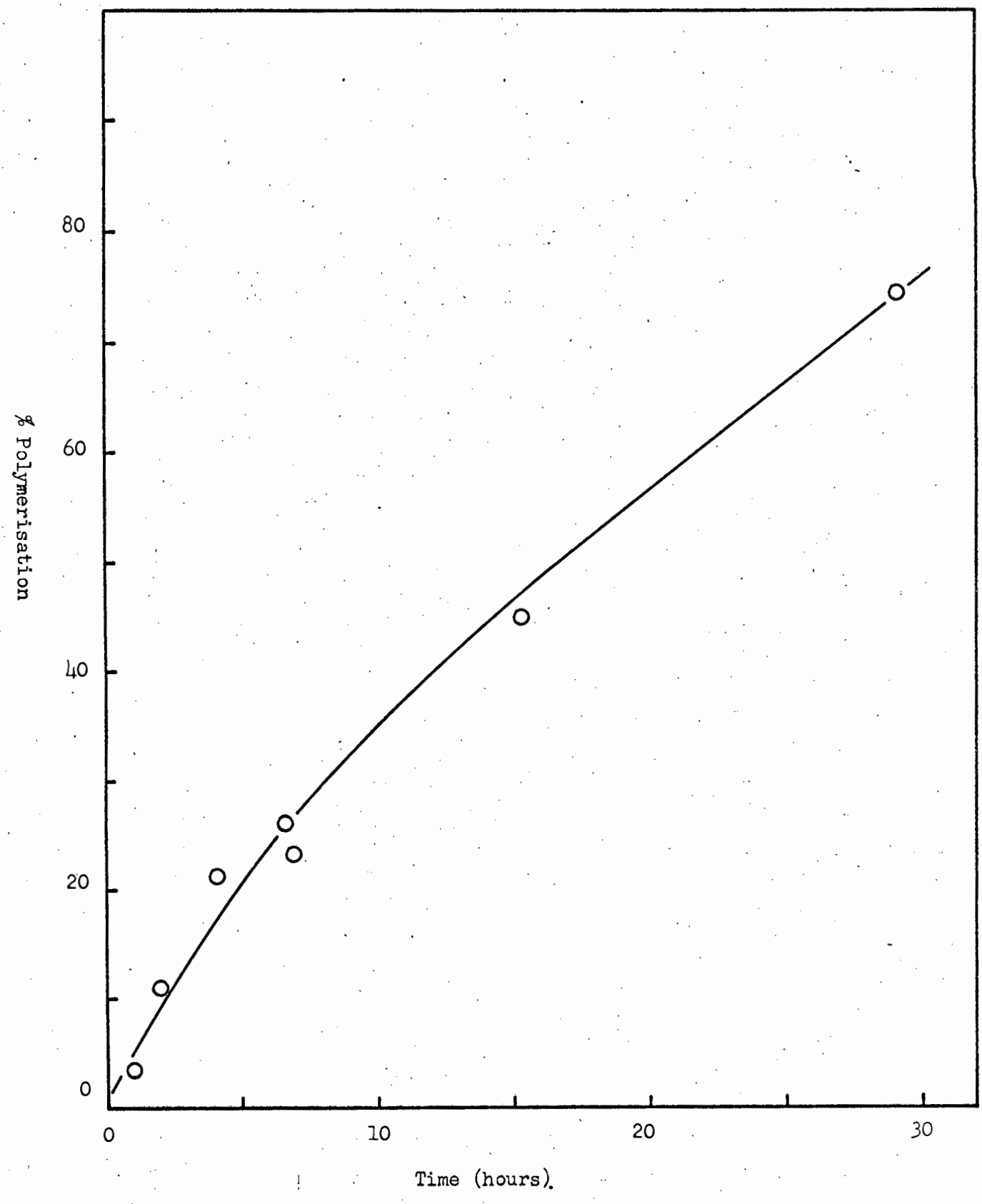


FIG. 4

EXTENT OF POLYMERISATION OF VINYLIDENE CHLORIDE AT 49°C WITH 0.3 MOLE % INITIATOR



2.5 The adsorption section of the apparatus.

This section of the apparatus was altered several times during the course of the experimental work. The original design (Fig. 5) was very simple, consisting of a section "C", containing a pressure gauge "G" and of known volume. Separated from this section, by means of a stopcock "A", was the thermostated reaction vessel "R". Also separated from section "C", by means of the stopcock "B" and immersed in the thermostat, was a flask "S" whose volume, including the base of the stopcock, had been determined by measuring the mass of water required to fill it. The volume of this flask was found to be 1075 ml ± 1 ml. The volume of the measuring section "C" and of the dead space above the adsorbent was determined by expanding dry nitrogen, at a known pressure, contained in the standard flask into the section whose volume was required at the temperature of the run.

2.5.1 Pressure gauges.

Various types of pressure gauges were tried. Mercury manometers were not used in the initial design because vinylidene chloride tends to interact with mercury, the surface of the mercury becoming coated with a white deposit. Membrane and Bourdon type gauges were therefore tested, these having to be made in the department. The final design, which was found to work satisfactorily, is shown in Figure 6. This gauge was calibrated over a small range of pressure difference across the membrane, the calibration curve being shown in Figure 7. The calibration curve was almost linear. This type of gauge was found to work satisfactorily but it was fragile and this limited the size of monomer aliquots which could be allowed to come into contact with the polymer.

FIG. 5

THE ADSORPTION SECTION OF THE APPARATUS

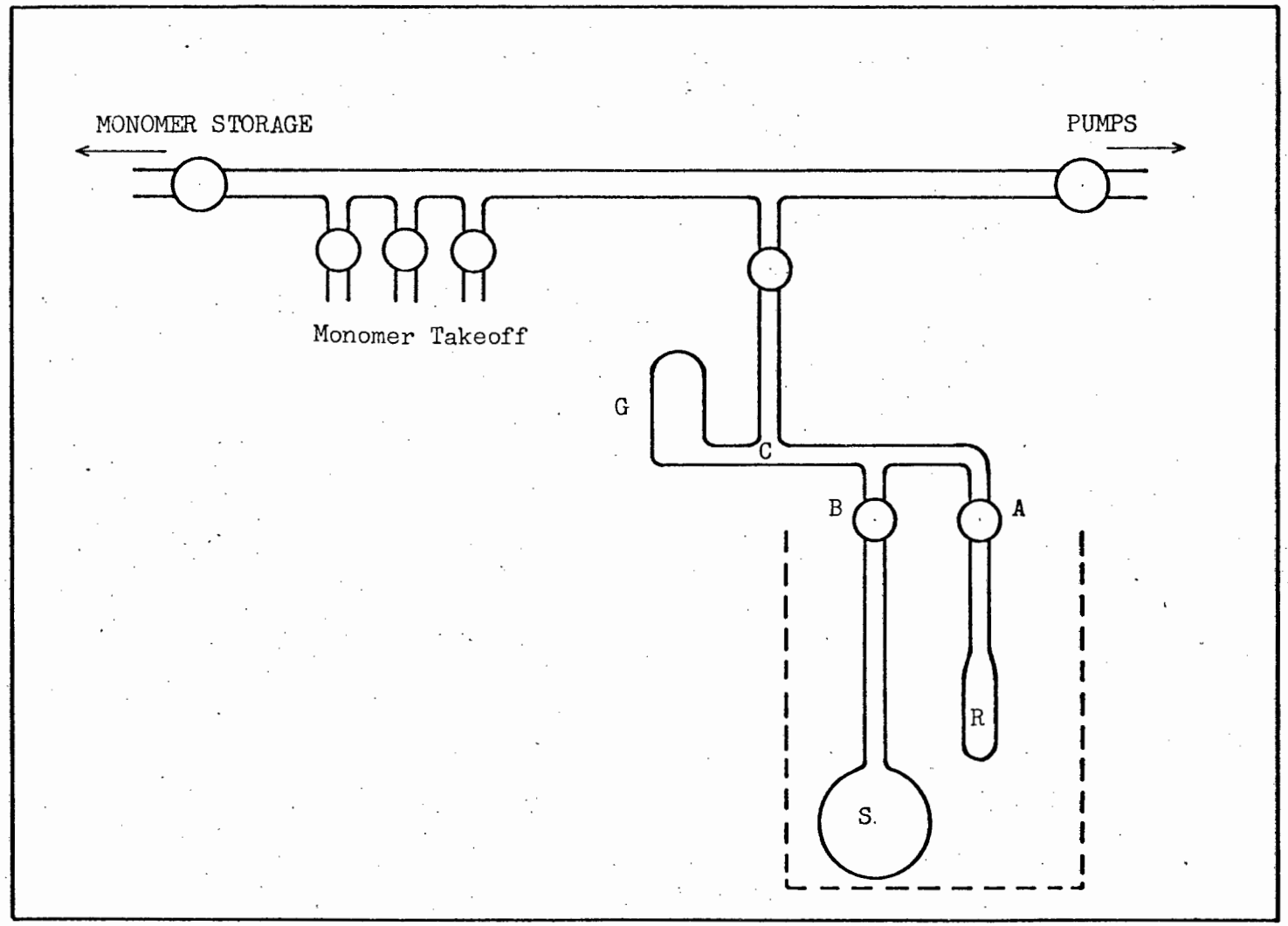


FIG. 6

BOURDON GAUGE

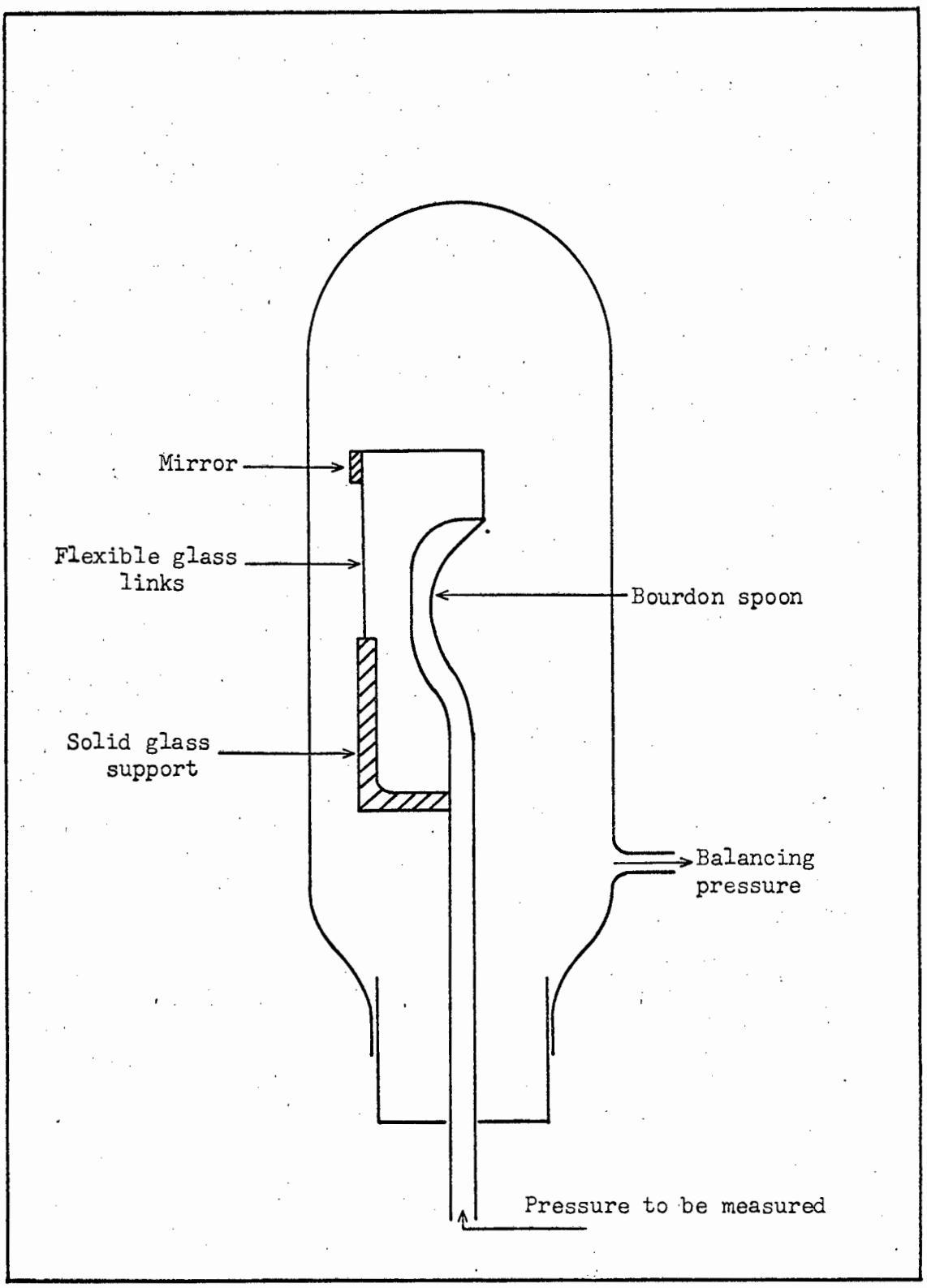
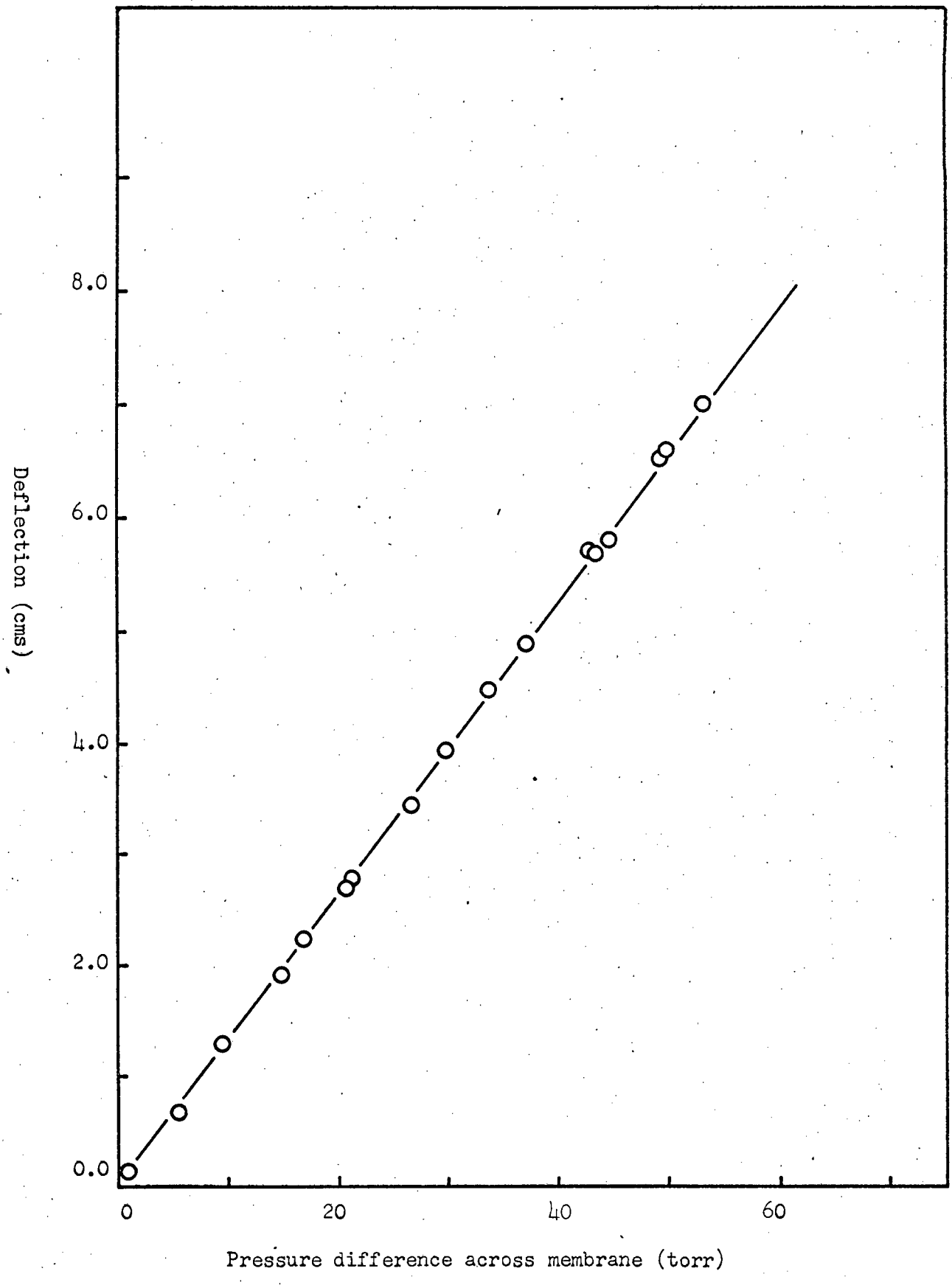


FIG. 7

CALIBRATION CURVE FOR BOURDON GAUGE.



2.5.2 Stopcock greases.

Four types of stopcock grease were available in the department. These were Apeazon L and M, Edwards high vacuum and silicone high vacuum grease.

Vinylidene chloride is known[4] to be soluble in hydrocarbon greases and therefore, in spite of its many disadvantages, silicone grease had to be used when this monomer was in the system. Edwards high vacuum grease was used for experiments involving vinyl chloride. However, it was observed that when either monomer was in the measuring section (section "C") there was always a pressure decrease before equilibrium was established. In some instances a pressure drop of as much as 10 torr was recorded on overnight standing. It seemed thus that the monomers were soluble to some extent in all the greases available and in later designs attempts were made to minimise this effect.

2.5.3 Measurement of the amount adsorbed.

The amount of monomer taken up by the polymer was measured by calculating the amount of monomer initially present in the measuring section, (section "C"), and that which remained in the combined measuring section and reaction vessel after the stopcock, separating them, had been opened and equilibrium had been established. The total volume of the combined sections was of the order of 200 ml, which was large and therefore no great precision could be expected in the final result. The first experimental studies were thus of a semi-quantitative nature, the more interesting aspects of which could be studied quantitatively in a better designed apparatus. (Section 3.3).

2.6 Temperature and pressure range.

The temperature range over which measurements were to be made

was a fairly narrow one, with an upper limit of 47°C and a lower limit of about 20°C, i.e., room temperature. Above 47°C the danger of the polymers decomposing becomes real. Below 20°C cooling baths would have had to be used and as the rate of monomer take up was slow, the level of these baths could not always be maintained constant; also the monomer vapours would show greater deviation from ideal behaviour and complicate the calculations. The pressure range was from 10 torr up to 600 torr because adsorption had been observed in this pressure range.(79)

2.7 Preliminary studies on the adsorption of vinyl chloride on polyvinyl chloride.

The apparatus with 2 g of polymer contained in the reaction vessel was degassed. Degassing was carried out by bringing the bath temperature to 47°C and then pumping until the pressure in the system, as recorded on the McCloud gauge, had fallen to 10^{-6} torr. Pumping was then continued for a further 8 hours and then the run was started.

After the apparatus and polymer had been degassed the measuring section was filled with monomer to the desired initial pressure. It was at this stage that it was noticed that the pressure in the section continued to fall for some time after the section had been disconnected from the monomer supply. (Section 2.5.3). Most of the pressure drop occurred in the first hour and thereafter only a small decrease in pressure was noted. The procedure adopted, therefore, was to leave the system to stand for one hour after the measuring section had been filled before taking the initial reading. The stopcock connecting the adsorption vessel to the measuring section was then opened and the monomer allowed to come into contact with the polymer.

It was realised that if the stopcock grease had taken up monomer, then when the pressure was reduced by expansion into the reaction vessel,

monomer could be released from the grease and this could lead to error in the calculated amount adsorbed at any time. However, at this stage it was decided to ignore these effects as only semi-quantitative results were expected.

2.7.1 Adsorption isotherms.

When the monomer was allowed to come into contact with the polymer, there was an immediate uptake of monomer followed by a much slower uptake. This slow process, in some instances at the higher pressures, continued for several days without equilibrium being established. It seemed therefore that the measurement of adsorption isotherms would be a lengthy and possibly an impossible task. Also reproducibility could be expected to be poor because if the adsorption process was slow, desorption is likely to be even slower, and hence degassing of the surface, particularly as it cannot be heated, would never be complete and the extent of degassing would vary from run to run. However, as this first series of experiments was only intended to be a preliminary investigation, the following procedure was adopted.

The surface was degassed as described above and the first aliquot of monomer was admitted and kept in contact with the polymer for 48 hours. After the 48 hours had elapsed, the next sample was admitted without degassing, i.e., the method of successive inlets was used. This sample was then allowed 48 hours to equilibrate and then the next sample added. In this way an isotherm was obtained. After the last sample had been admitted and allowed to equilibrate, the polymer was degassed and a large aliquot admitted and allowed to equilibrate for 48 hours. In all cases the result for the large aliquot fell below the isothermal curve for a series of small aliquots.

The isotherms obtained plotted as amount adsorbed (ml N.T.P.)

against pressure are shown in Figure 8. If the results are plotted as log amount adsorbed against log pressure as in Figure 9, straight lines result indicating that over the pressure range studied the isotherms obey the Freundlich equation.

An estimate of the isosteric heats of adsorption was obtained for different amounts adsorbed on the surface from the slopes of the log equilibrium pressure against reciprocal of the absolute temperature plots. (Fig. 10). A plot of heat of adsorption against log amount adsorbed (Fig.11) seemed linear as would be expected if the Freundlich isotherm was obeyed.[49,50]

2.7.2 Thermal cycling.

Because of the slow rate of adsorption and therefore the long periods of time required to obtain a set of isotherms, a method first used by Frankenburg[33] was tested. Frankenburg allowed the adsorbate to equilibrate with the adsorbent at the highest temperature at which measurements were to be made. When equilibrium had been established the system was cooled to the next temperature and he found that equilibrium was established instantaneously at the lower temperature. After the amount adsorbed at the lowest working temperature had been obtained, the temperature was raised again to the original value. On reaching this temperature it was found that equilibrium was instantaneous, the amount adsorbed, within experimental error, being the same as that which had been previously adsorbed at this temperature.

The danger in this method is that if two processes with different activation energies are operating then the one of higher activation energy may not be significant at the lower temperature, but significant at the higher temperature; therefore if equilibrium is established at the higher temperature and the system cooled to the lower,

FIG. 8

ADSORPTION ISOTHERMS FOR VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE

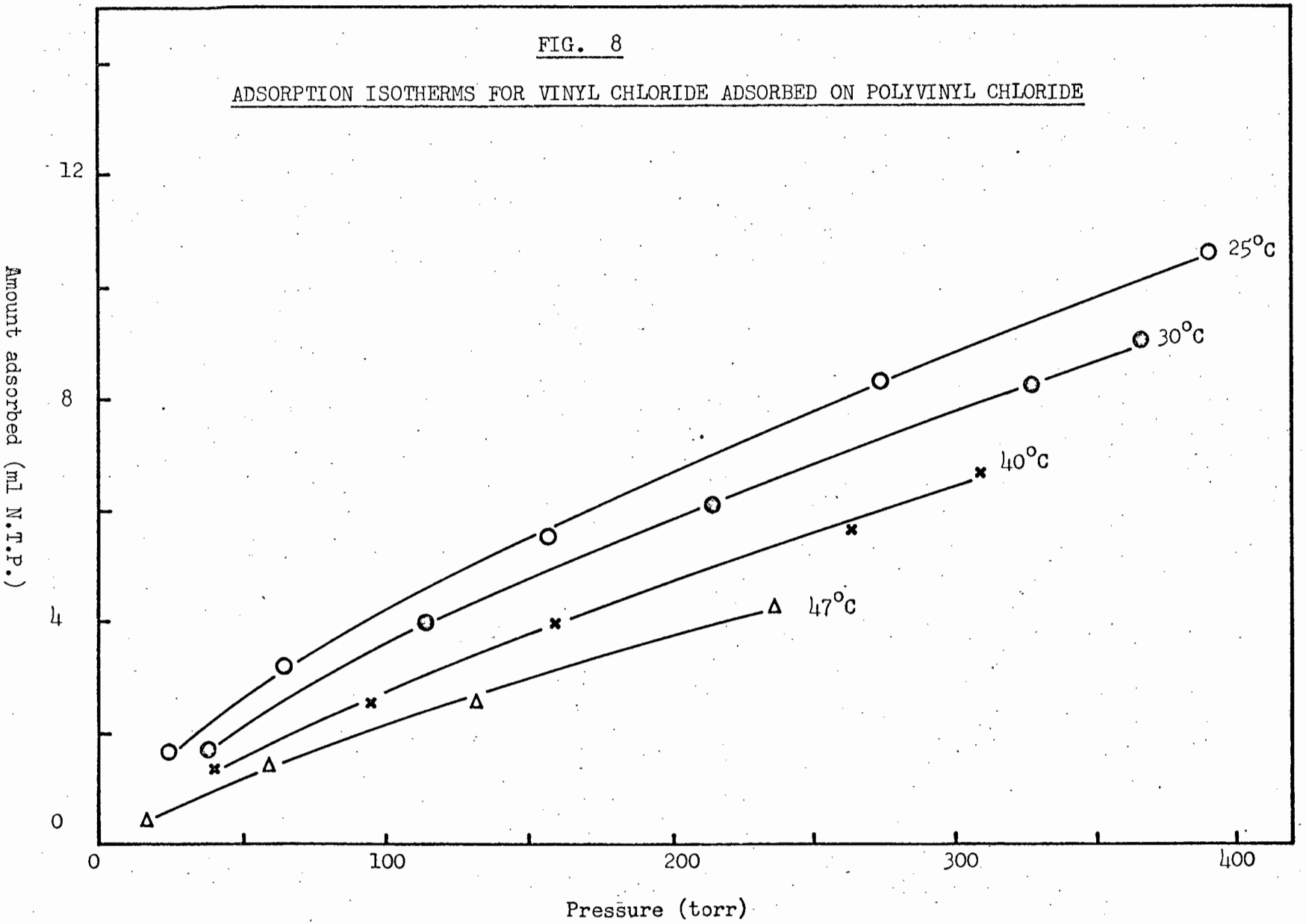


FIG. 9

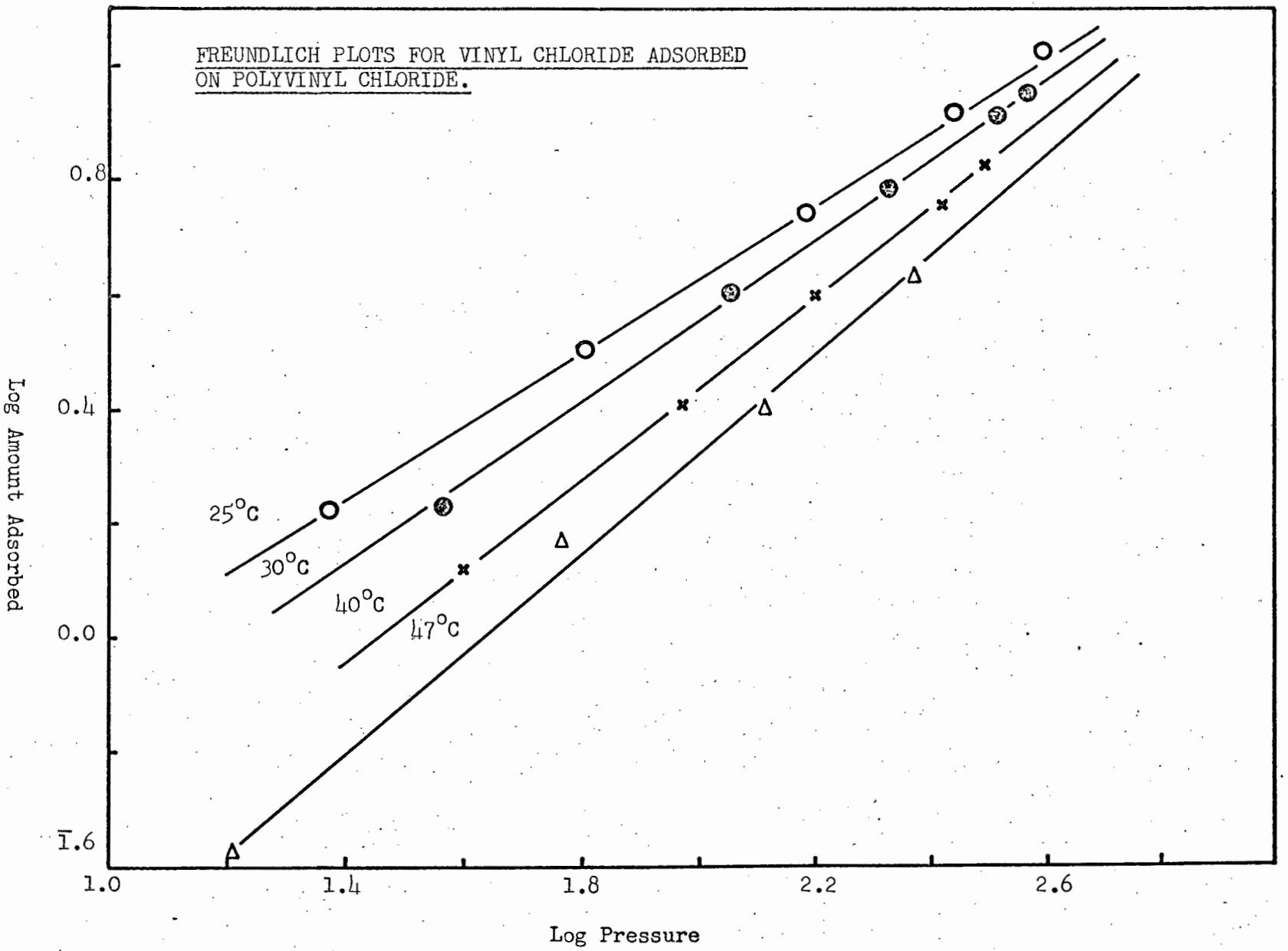

FREUNDLICH PLOTS FOR VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE.
0.8
0.4
0.0
$\bar{1}.6$
Log Amount Adsorbed
25°C
30°C
40°C
47°C
1.0
1.4
1.8
2.2
2.6
Log Pressure

FIG. 10

ISOSTERES FOR VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE

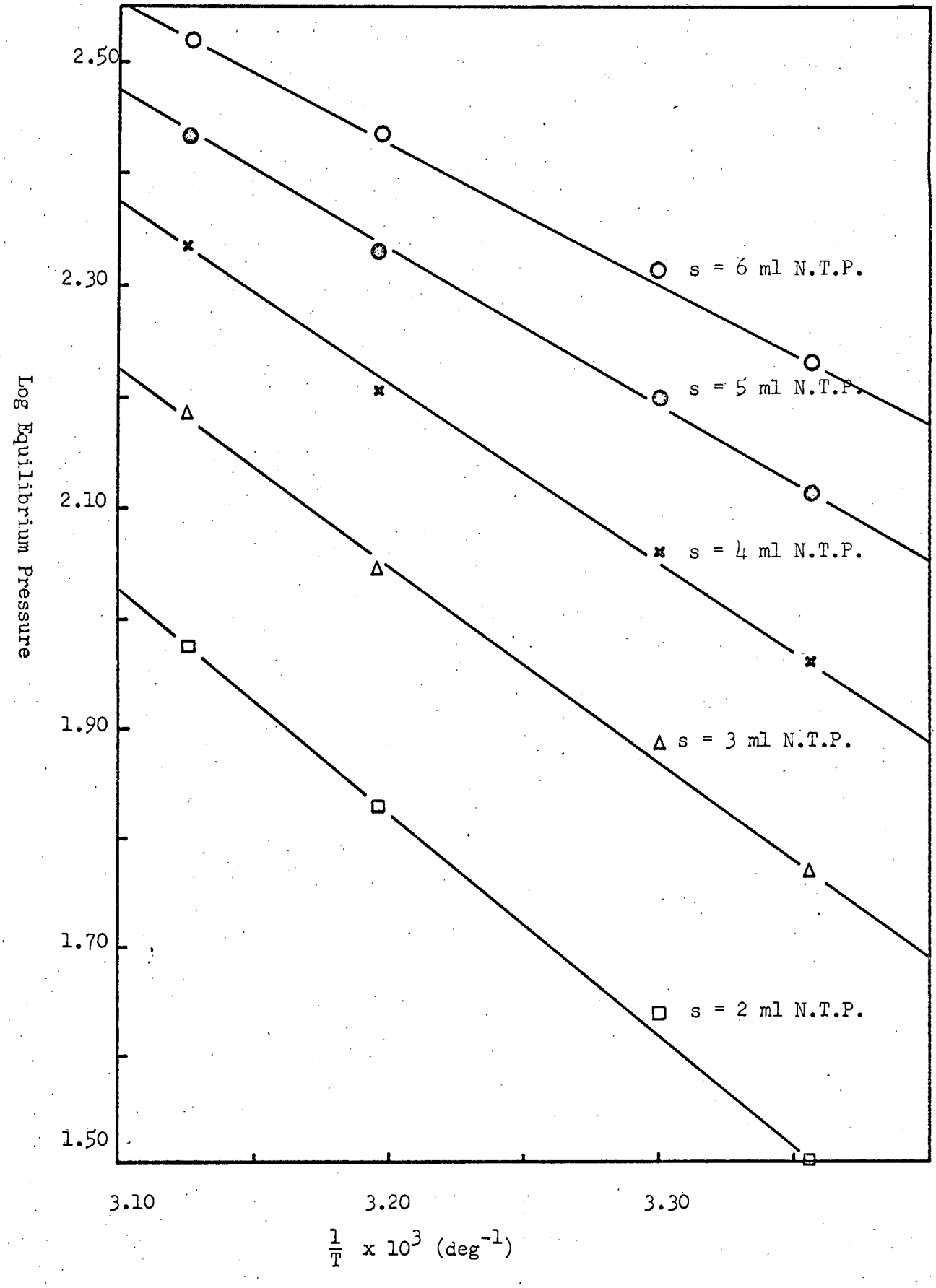
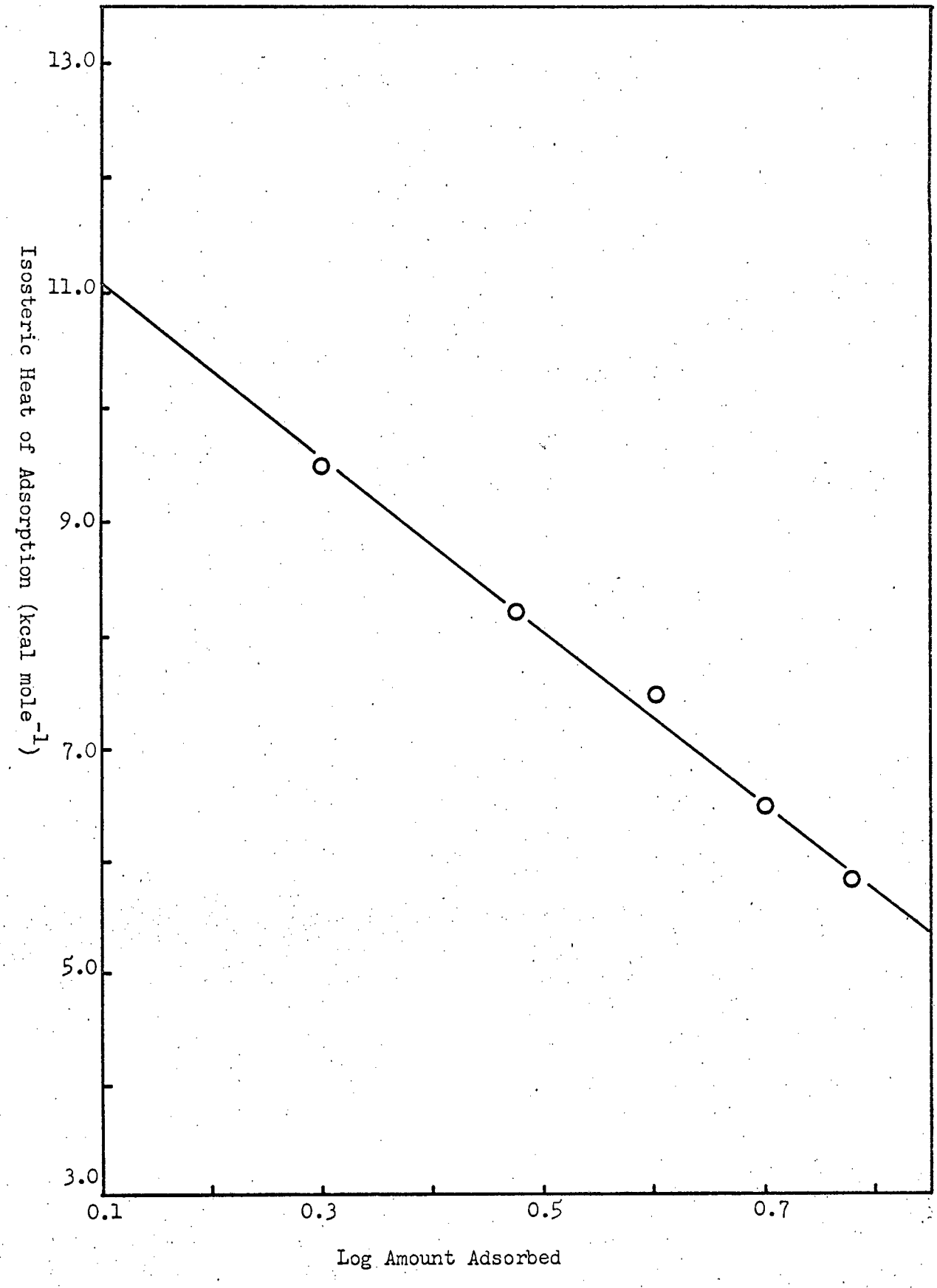


FIG. 11

VARIATION OF THE ISOSTERIC HEAT OF ADSORPTION WITH SURFACE COVERAGE FOR VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE



adsorbate taken up by the slow process at the higher temperature will not desorb but will remain on the surface. This will lead to an amount adsorbed at the lower temperature in excess of the true equilibrium value. The following experiment was performed to check this.

Monomer was allowed to come into contact with the polymer at the lowest temperature, viz., 25°C. The system was allowed to stand until the pressure remained steady for 5 hours. The temperature was then raised to 50°C and held at that temperature until the pressure remained steady for 5 hours. The temperature was then lowered to the original value of 25°C and held there until the pressure remained steady for 5 hours. The initial amount of monomer and the final amount of monomer adsorbed at 25°C were then compared. The results of this experiment are shown in Table I.

Table I shows clearly that at higher pressures more monomer is adsorbed if Frankenburg's method is used than would be if the monomer were allowed to equilibrate at 25°C. Two further observations that were made in the course of this experiment were that:

(a) the net effect of raising the temperature was that monomer was desorbed, i.e., more monomer is taken up at 25°C than at 50°C;

(b) on returning the temperature to the lower value equilibrium is established almost immediately.

2.7.3 Rate of adsorption.

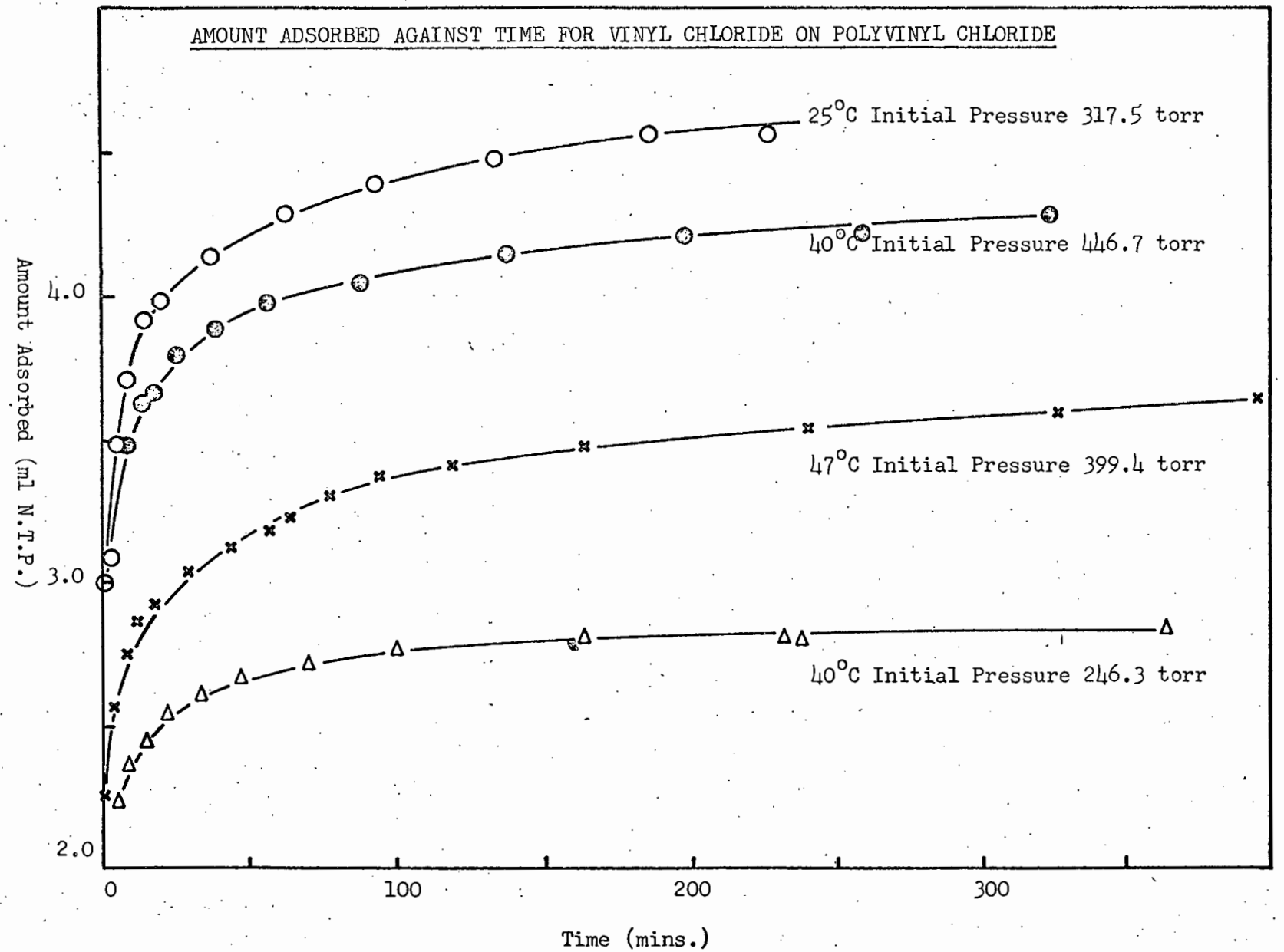
The rate of uptake of monomer was studied by allowing monomer to come into contact with the freshly evacuated polymer and measuring the amount adsorbed at various times after the admission. Plots of amount adsorbed against time for some of the runs are shown in Figure 12. In all cases there was a rapid initial uptake of monomer followed by a slower measurable process.

TABLE I.

Effect of Thermal Cycling on Amount of Monomer Adsorbed at 25°C.

Initial equilibrium pressure at 25°C	Amount initially adsorbed at 25°C	Amount finally adsorbed at 25°C	Difference
(torr)	(ml N.T.P.)	(ml N.T.P.)	(ml N.T.P.)
3.4	0.15	0.15	0.00
5.7	0.33	0.33	0.00
14.3	0.63	0.64	0.01
24.4	0.91	0.93	0.02
44.4	1.38	1.46	0.08
77.8	2.13	2.34	0.21
187.9	3.98	4.50	0.52

FIG. 12


AMOUNT ADSORBED AGAINST TIME FOR VINYL CHLORIDE ON POLYVINYL CHLORIDE
25°C Initial Pressure 317.5 torr
40°C Initial Pressure 446.7 torr
47°C Initial Pressure 399.4 torr
40°C Initial Pressure 246.3 torr
Amount Adsorbed (ml N.T.P.)
4.0
3.0
2.0
0
100
200
300
Time (mins.)

2.8 Preliminary studies of the adsorption of vinylidene chloride on polyvinyl chloride.

As vinylidene chloride is known to dissolve in hydrocarbon greases[4] silicone high vacuum grease had to be used for stopcock lubrication when this monomer was in the system. This grease gave a certain amount of trouble inasmuch as it tended to "creep" from its area of application into other regions of the apparatus. If it became necessary to do any glassblowing in the vicinity of the grease large sections had to be removed and replaced because the grease decomposed under the heat of the glassblower's torch. It also tended to block small bore stopcocks and this, together with its rather poor holding power, meant that stopcocks had to be cleaned and regreased on the average of once every three or four days. It was also observed that even silicone grease tended to dissolve vinylidene chloride to some small extent.

2.8.1 Adsorption isotherms.

The same sample of polyvinyl chloride as was used for the vinyl chloride studies was used in this series of experiments. Because of the long periods required to attain equilibrium and the inability of the apparatus to remain leakproof over this long period, Frankenburg's method was employed to obtain some measure of the equilibrium characteristics of the system. Monomer was admitted to the polymer at 47.1°C and the system allowed to equilibrate for 48 hours. The temperature was then reduced stepwise to 37.5°C and 27.8°C. At these temperatures equilibrium was attained almost instantaneously. On raising the temperature again to 47.1°C, equilibrium was quickly established and within experimental error the amount adsorbed on returning to the higher temperature was the same as that initially adsorbed at this temperature. The next sample was then admitted and the procedure repeated. The pressure range over which these

isotherms was measured was a very narrow one, 20 torr to 120 torr, this because of the difficulty of keeping the system leakproof. These three isotherms are shown in Figure 13, in which "amount taken up" is plotted against pressure. If the log of the amount taken up is plotted against log pressure, straight lines result as shown in Figure 14.

Plots of log equilibrium pressure against the reciprocal of the absolute temperature at constant amount adsorbed, were made and these were found to be linear (Fig. 15). From the slope of these plots the isosteric heats of adsorption could be determined and these were found to vary from 10.4 k cal/mole at 2 ml adsorbed to 9.3 k cal/mole at 4 ml adsorbed.

2.8.2 Rate of adsorption.

Figure 16 shows a plot of amount adsorbed against time, the results being obtained using the method already described for vinyl chloride. The main characteristics of these runs were very similar to those described for vinyl chloride, i.e., there was a very large initial uptake of monomer followed by a much slower process.

2.9 The adsorption of vinylidene chloride on polyvinylidene chloride.

The polymer was prepared as described earlier (Section 2.4). A sample weighing 19.5 g was used in experiments with this system. Difficulty was experienced in degassing the sample and when left overnight the pressure always rose to 1 torr. After the series had been completed the sample tube was opened and a very strong acid smell was noticed. It seems very likely that the polymer is not stable and decomposes somewhat under the experimental conditions. There were also signs that the monomer, when left in the apparatus, tended to polymerise, initiated by light. To overcome this, that section of the apparatus which contained the monomer was painted black. Because of these complications only a few rate runs were performed

FIG. 13

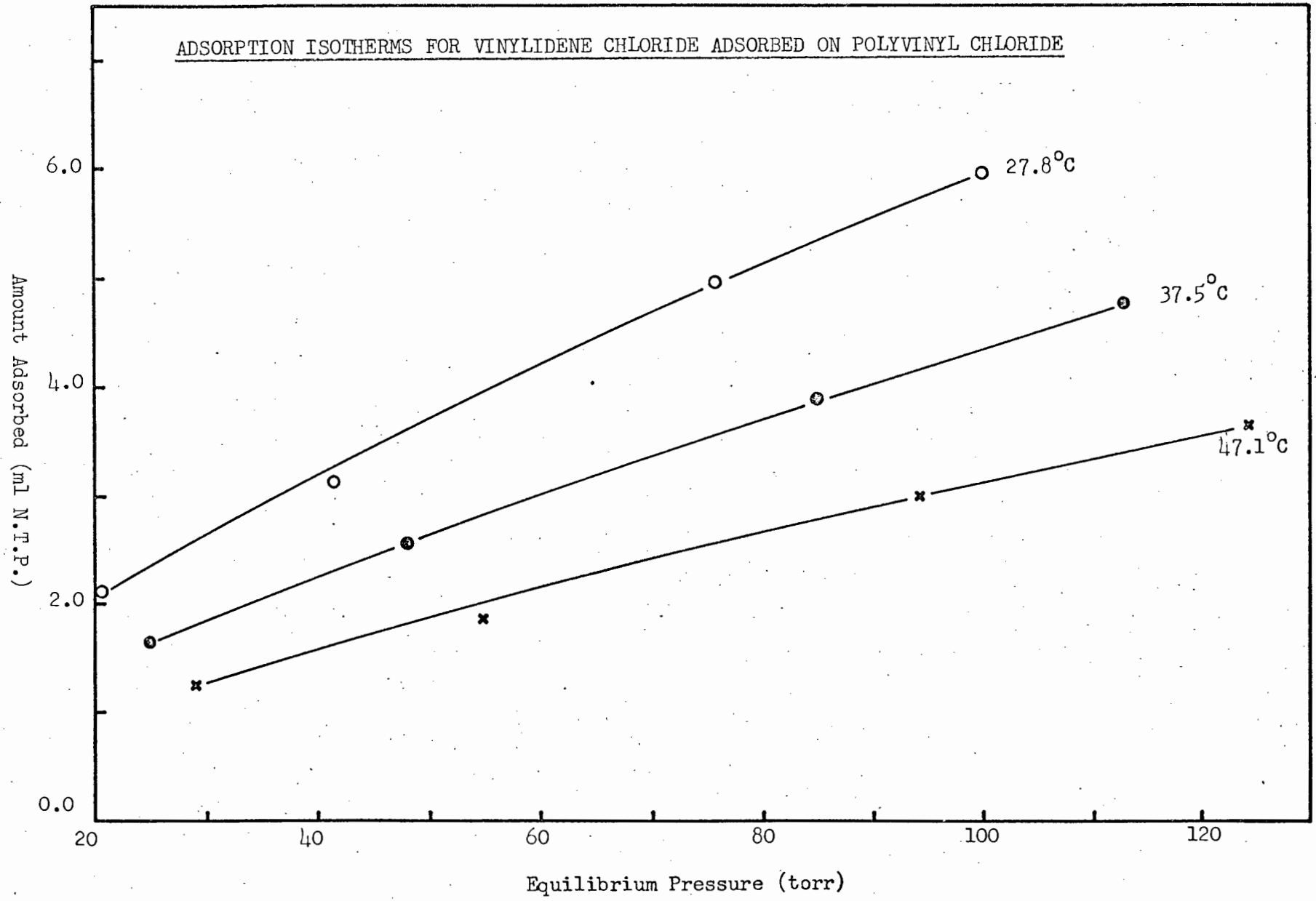

ADSORPTION ISOTHERMS FOR VINYLIDENE CHLORIDE ADSORBED ON POLYVINYL CHLORIDE
27.8°C
37.5°C
47.1°C
Amount Adsorbed (ml N.T.P.)
0.0
2.0
4.0
6.0
20
40
60
80
100
120
Equilibrium Pressure (torr)

FIG. 14

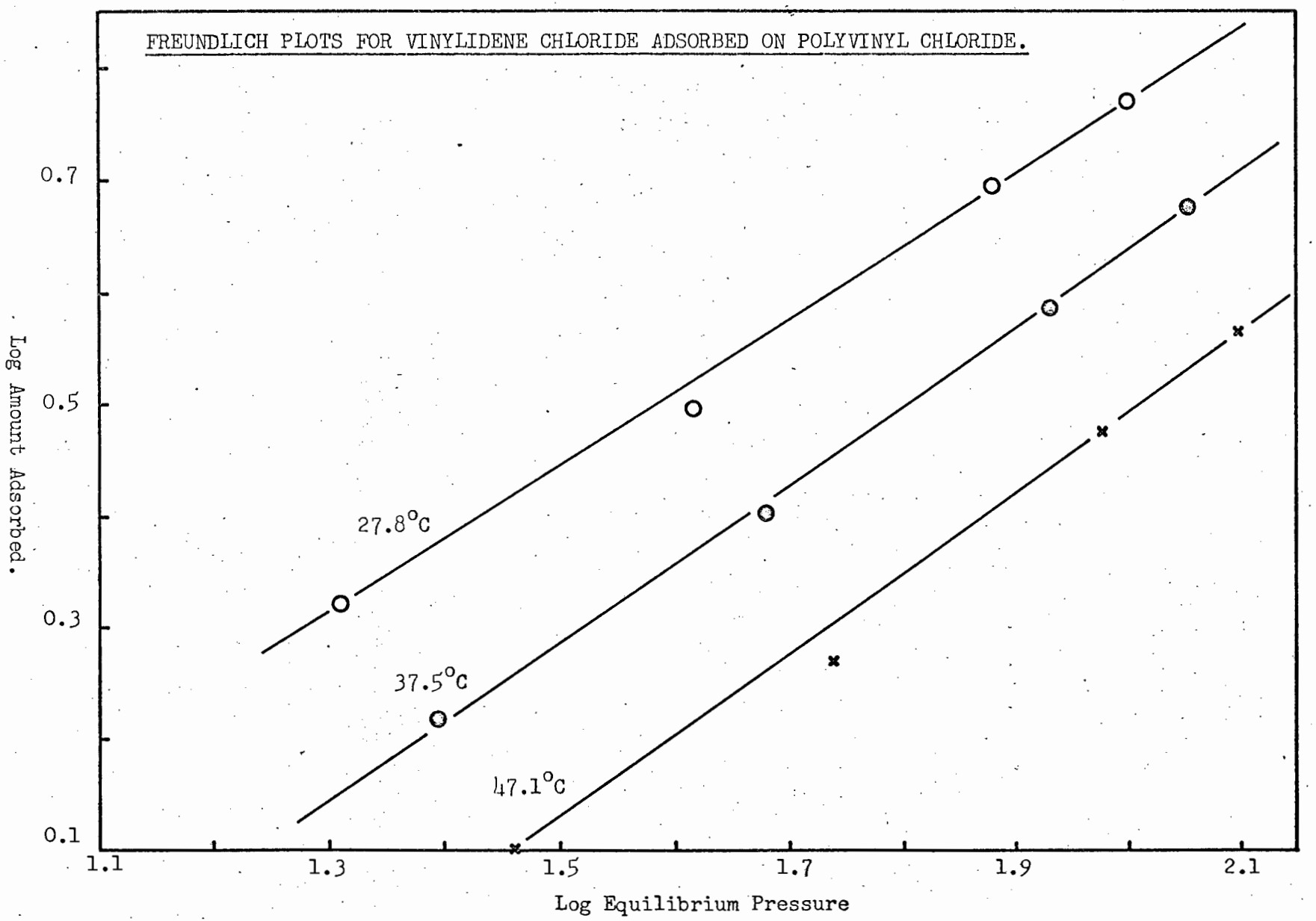
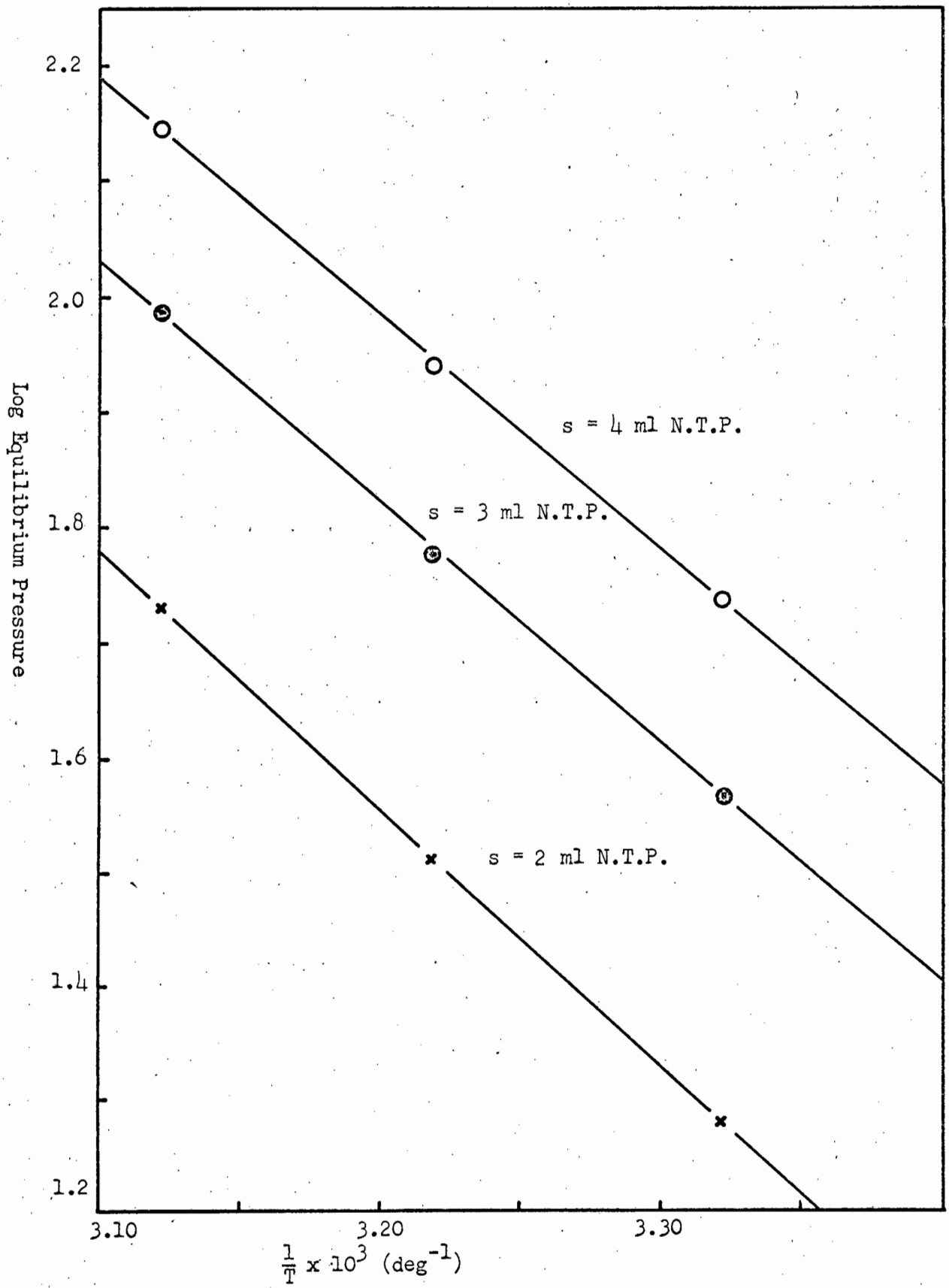

FREUNDLICH PLOTS FOR VINYLIDENE CHLORIDE ADSORBED ON POLYVINYL CHLORIDE.
0.7
0.5
0.3
0.1
Log Amount Adsorbed.
27.8°C
37.5°C
47.1°C
1.1
1.3
1.5
1.7
1.9
2.1
Log Equilibrium Pressure

FIG. 15

ISOSTERES FOR VINYLIDENE CHLORIDE ADSORBED ON POLYVINYL CHLORIDE



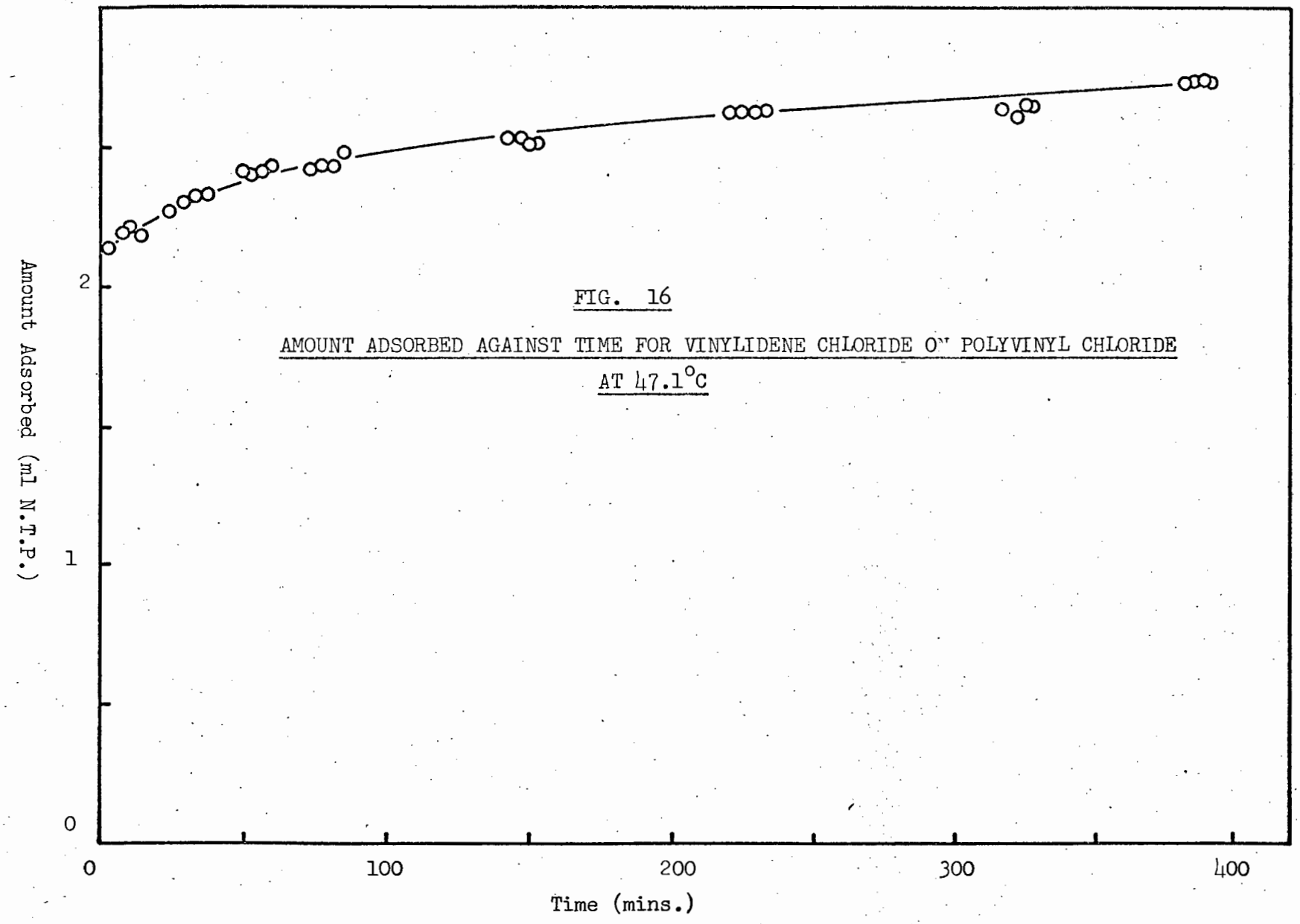


FIG. 16

AMOUNT ADSORBED AGAINST TIME FOR VINYLIDENE CHLORIDE ON POLYVINYL CHLORIDE AT 47.1°C

on this system and these are shown in Figure 17. In these runs it was found that the amount of monomer adsorbed was less than for the other systems; also the initial fast takeup was small, most of the adsorption occurring at a measurable rate.

2.10 Conclusions drawn from preliminary survey.

The preliminary studies indicate that generally the systems investigated behave similarly. The heats of adsorption estimated from the isotherms are of the same order of magnitude. The rate studies indicate that there seem to be at least two processes occurring; a very fast initial uptake of monomer which seems to be unactivated, or of low activation energy, and thermally reversible and a very much slower activated process. This slow process makes the measurement of adsorption isotherms a lengthy and imprecise process.

These deductions lead to the conclusion that:

(i) A study of the kinetics of the adsorption will be easier and more fruitful than equilibrium studies.

(ii) One of the systems should be chosen and studied in detail.

2.10.1 The choice of system for more detailed study.

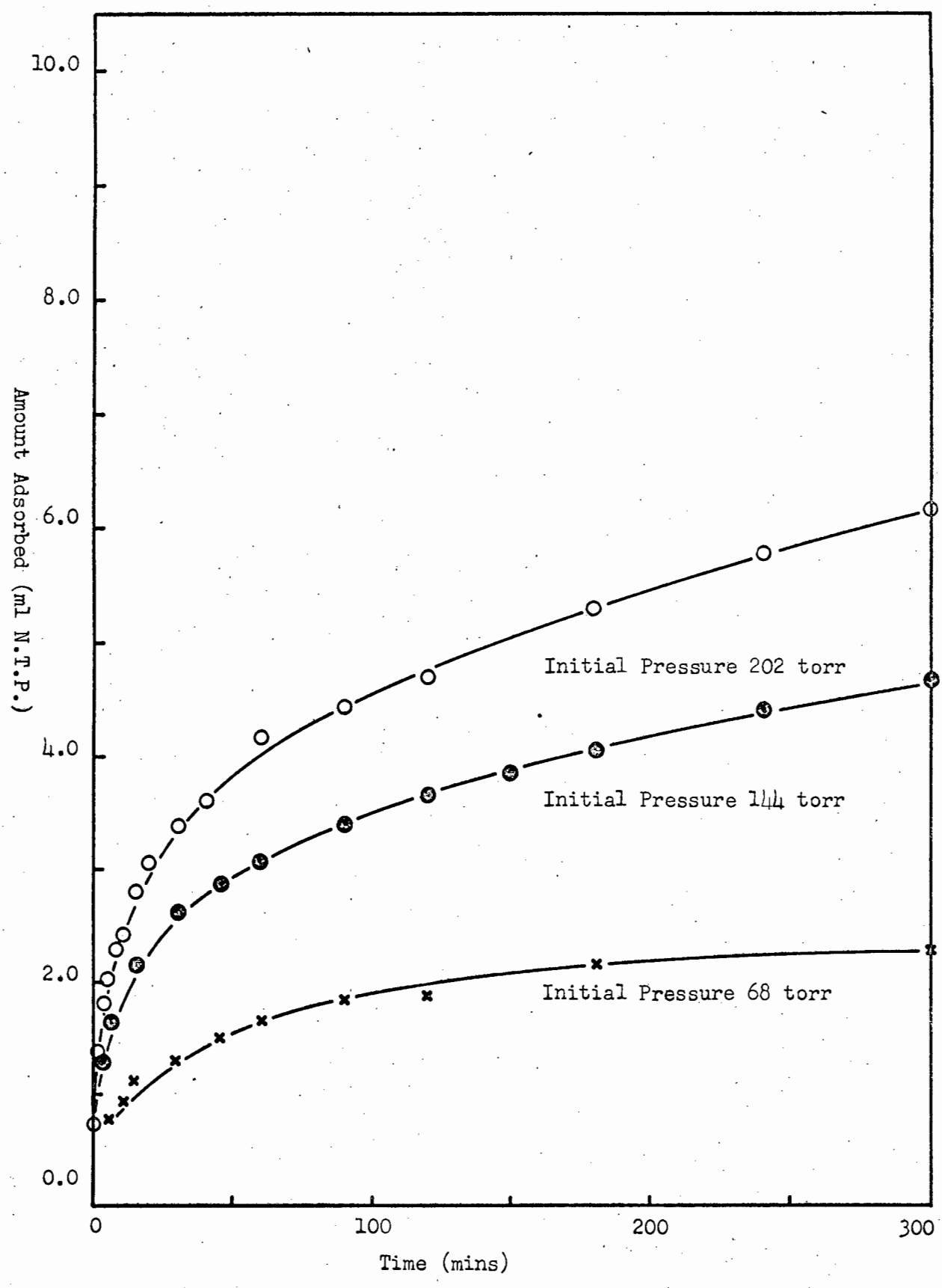
The system vinyl chloride adsorbed on polyvinyl chloride was selected for further study for the following reasons:

(i) Mercury can be used with vinyl chloride and therefore mercury manometers can be used for pressure measurement instead of the fragile membrane type gauges. Also gas burettes using mercury can be employed.

(ii) Vinyl chloride does not tend to polymerise in the apparatus even when exposed to light.

FIG. 17

AMOUNT ADSORBED AGAINST TIME FOR VINYLIDENE CHLORIDE ON POLYVINYLIDENE CHLORIDE AT 42.2°C



(iii) Polyvinyl chloride shows fewer signs of decomposing than does polyvinylidene chloride.

(iv) It might be possible to use hydrocarbon greases with vinyl chloride instead of the more troublesome silicone grease.

C H A P T E R III

EXPERIMENTAL II

The Adsorption of Vinyl Chloride on Polyvinyl Chloride.

The following will be described in this section:

(i) The uptake of monomer by stopcock grease.

(ii) The effect on the course of the reaction of sudden changes in pressure.

(iii) The course of the reaction at constant pressure.

(iv) The course of the reaction at constant volume.

(v) The effect on the course of the reaction on changing from conditions of constant pressure to conditions of constant volume.

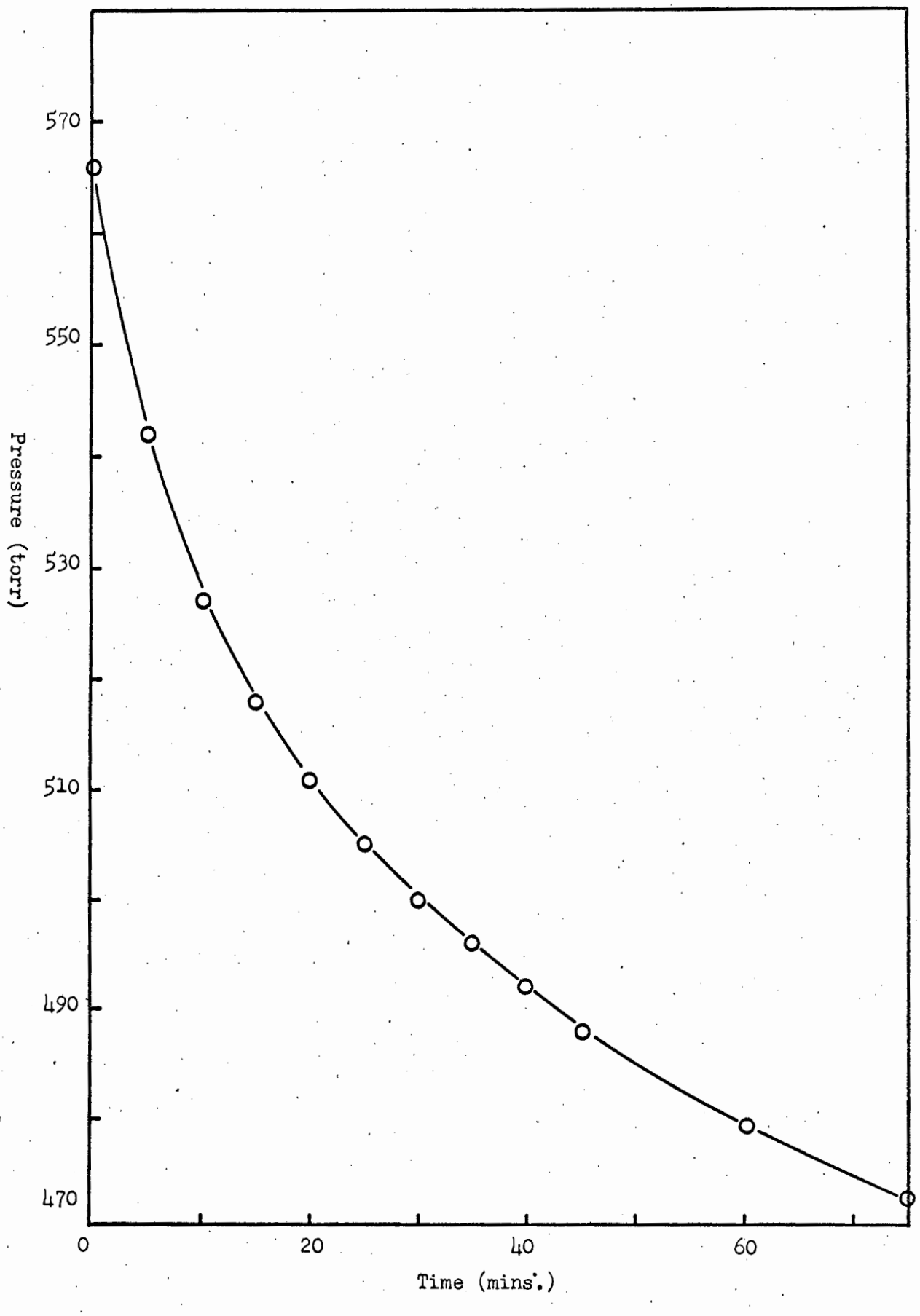
(vi) Adsorption isotherms.

3.1 The uptake of monomer by stopcock grease.

The tendency for the stopcock grease to take up monomer has already been mentioned (Section 2.5.2) and it was realised that some effort must be made to eliminate this source of error, or at least to minimise its effect. The first attempt was to replace the conventional type stopcocks with "Springham greaseless" high vacuum stopcocks. These were found to be considerably worse than the conventional type of stopcock. The pressure of a sample of monomer enclosed between five of these stopcocks fell from 630 torr to 450 torr over a period of 12 hours. It was suspected that the monomer was being taken up by the neoprene membranes of these stopcocks. To test this hypothesis a sample of nitrile rubber was placed in contact with monomer and the pressure followed on a mercury manometer. Over a period of 18 hours the pressure fell by approximately 180 torr (Fig. 18). Replacing the vessel containing the rubber by one containing glass wool resulted in no pressure change over a period of 24 hours. Similarly vinyl chloride vapour, in contact with benzoyl peroxide solid at room temperature, suffered no drop in pressure over a period of three hours, in spite of the fact that benzoyl peroxide initiates the liquid phase polymerisation.

FIG. 18

ADSORPTION OF VINYL CHLORIDE BY NITRILE RUBBER



The five greaseless stopcocks were replaced by five conventional stopcocks greased with Edwards high vacuum grease and the region enclosed between them filled with monomer vapour. The pressure in this region fell steadily as shown in Figure 19. After 45 minutes had elapsed, the pressure having fallen by about 10 torr, the pressure in the system was reduced by removing monomer from the section. There followed a steady increase of pressure indicating desorption (Fig. 20). The other hydrocarbon greases all behaved similarly and it seemed likely that all hydrocarbon greases would take up vinyl chloride to some extent.

As it did not seem possible to avoid grease takeup completely, except by using mercury cut-offs, which would have been inconvenient, an attempt was made to minimise this grease effect by designing the apparatus such that the number and size of the stopcocks, in contact with the monomer, was reduced to a minimum.

One way in which the number of stopcocks could be reduced to two is shown in Figure 21. With the stopcock B in the position shown in Figure 21(a) monomer could be admitted to the apparatus through stopcock A. The monomer could be brought into contact with the polymer by rotating stopcock B into the position shown in Figure 21(b). From the known values for the volumes D, E and R and the pressures recorded on the manometer the amount taken up could be calculated.

The apparatus was now altered so that this modification could be tested. With the stopcock B in the position shown in Figure 21(a) the section was filled with monomer and the pressure variation with time followed by means of the manometer (Fig. 22). The total change of 5 torr represented an amount of monomer equivalent to approximately 0.1 ml at N.T.P. After the 17 hour period had elapsed the monomer was expanded into a blank reaction vessel by rotating stopcock B into the position shown in Figure 21(b).

FIG. 19

ADSORPTION OF VINYL CHLORIDE MONOMER ON STOPCOCK GREASE

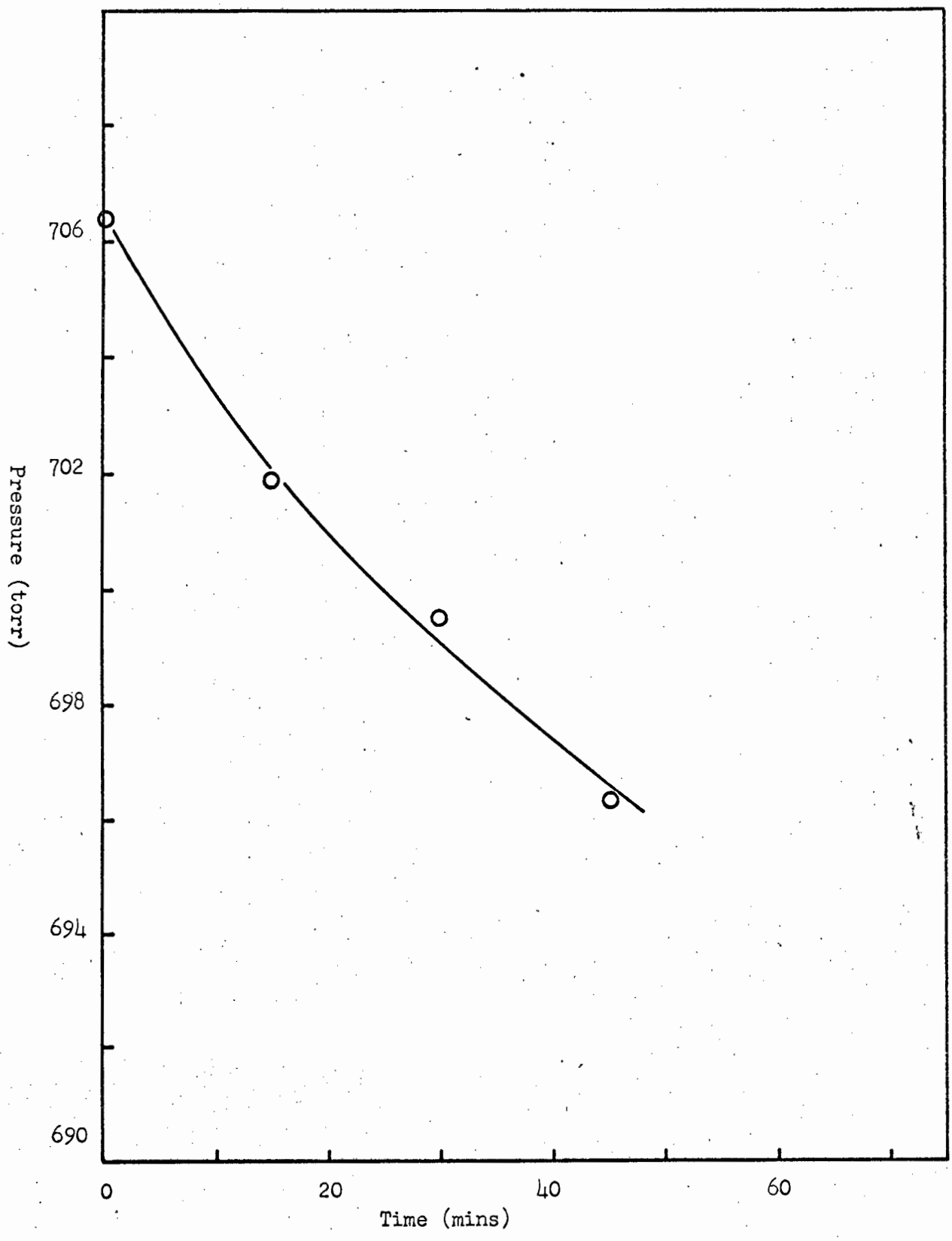


FIG. 20

DESORPTION OF VINYL CHLORIDE MONOMER FROM STOPCOCK GREASE

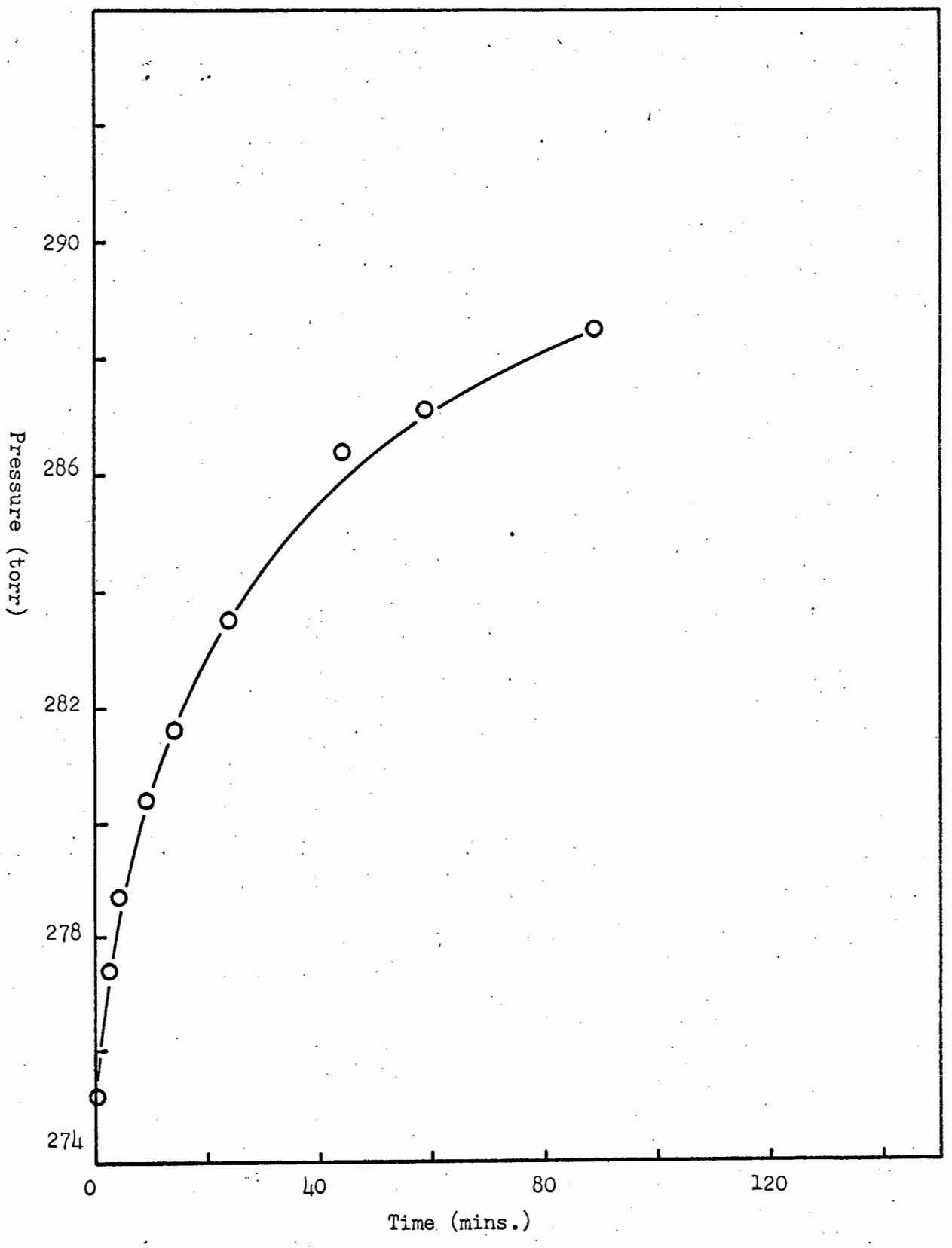


FIG. 21

MODIFIED APPARATUS FOR MINIMIZING THE NUMBER OF STOPCOCKS

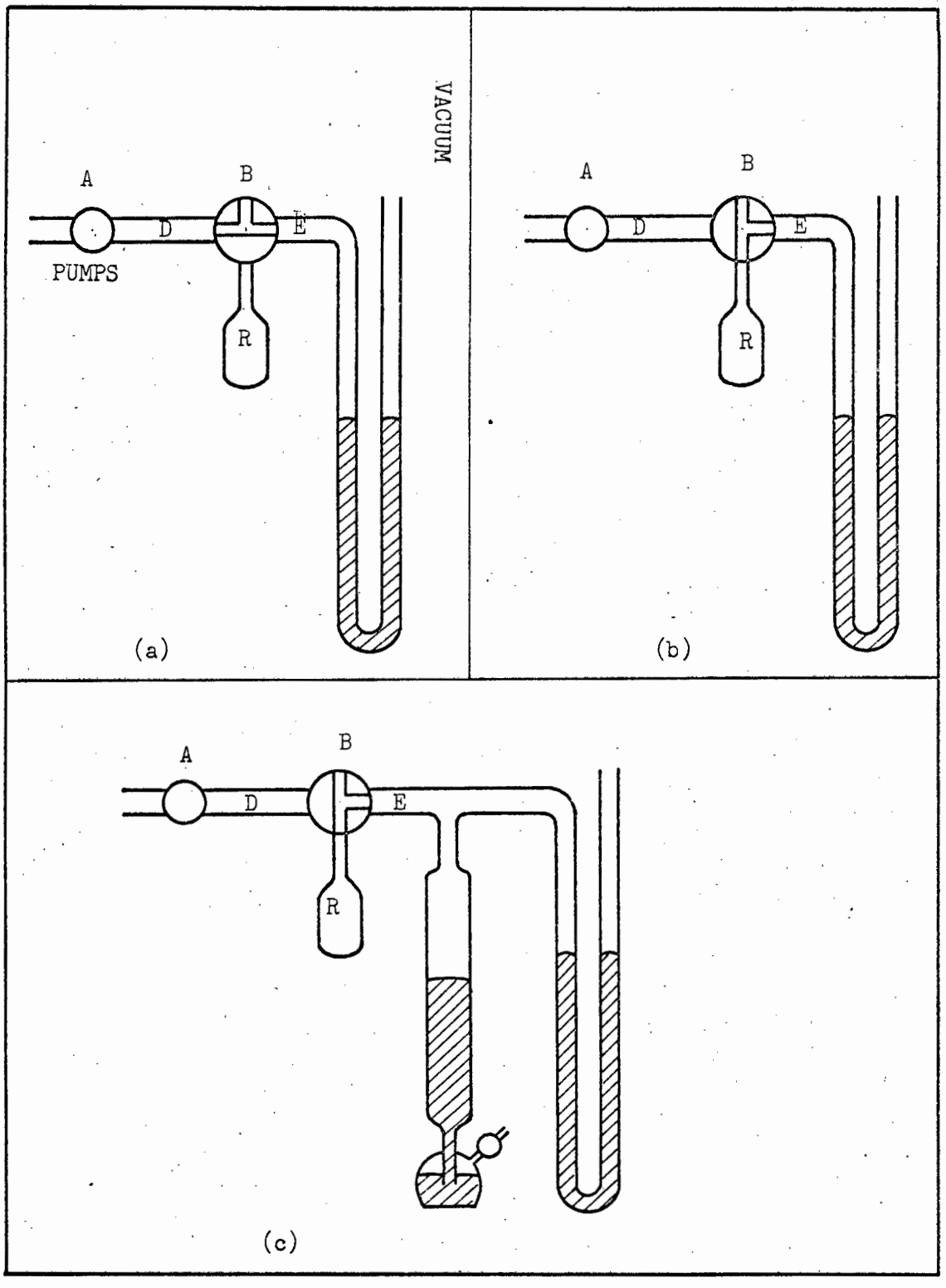
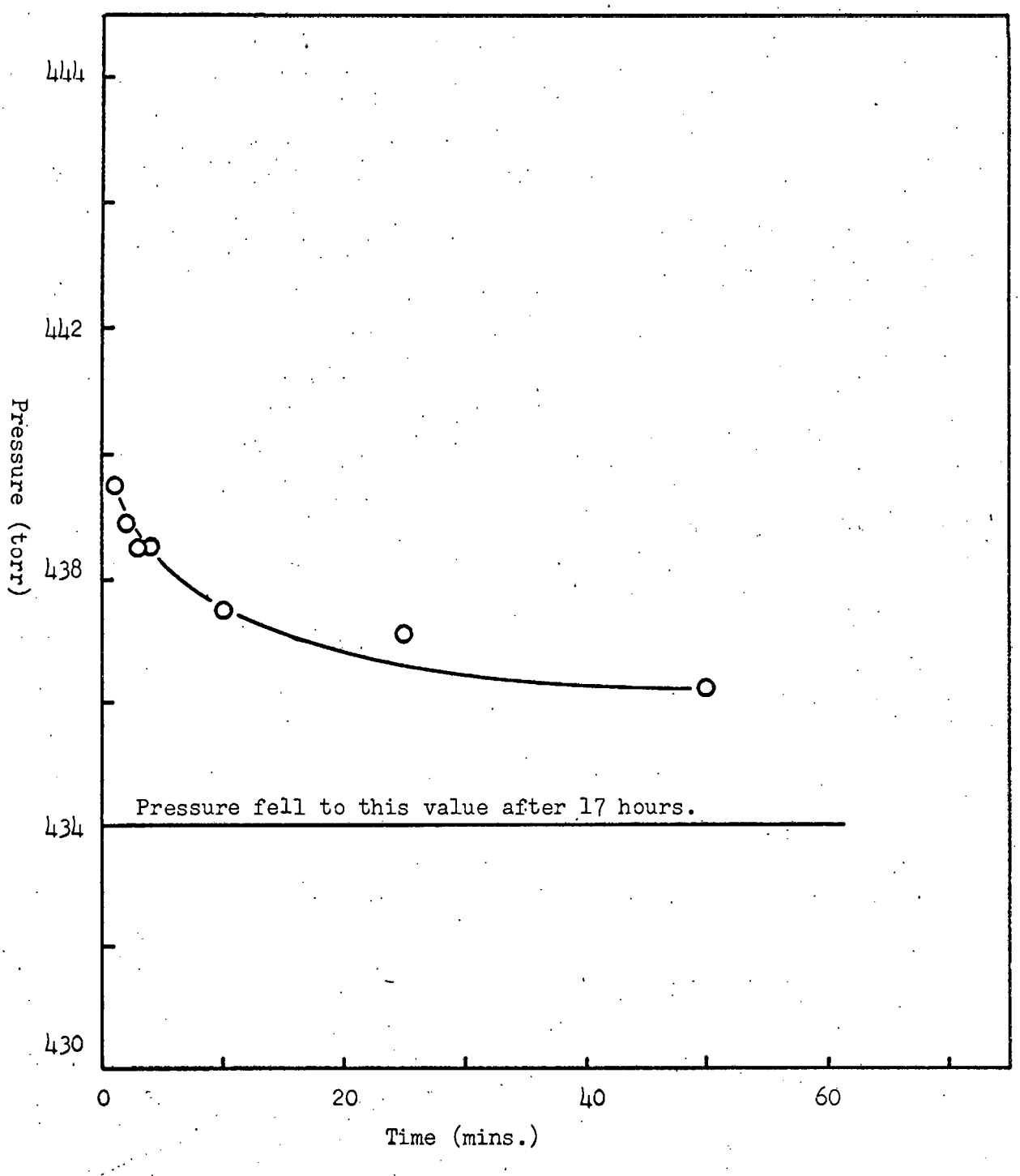


FIG. 22

VARIATION OF PRESSURE WITH TIME FOR VINYL CHLORIDE MONOMER IN CONTACT WITH STOPCOCK GREASE IN THE MODIFIED APPARATUS



After expansion it was found that no further pressure change occurred, the pressure remaining constant over a period of 375 minutes.

One further modification was made to the apparatus; a gas burette was added between the manometer and stopcock B as shown in Figure 21(c). The purpose of the gas burette was to enable the pressure in the system to be altered during the course of the reaction without having to add monomer. The apparatus volumes were then calibrated with dry nitrogen. Having calibrated the apparatus, it was considered wise to do one more experiment to investigate the effect of the stopcock grease on monomer takeup when the pressure in the system was altered. The degassed system with stopcock B in the position shown in Figure 21(a) was filled with monomer and left for 24 hours. After 24 hours had elapsed the pressure in the section was measured and the amount of gaseous monomer present determined. The pressure was then increased stepwise by raising the mercury in the gas burette and calculating the amount of gaseous monomer present after each step. The results tabulated in Table 2 indicate that within experimental error no monomer disappears.

It can be concluded that there is a definite takeup of monomer vapour by the stopcock grease, but that the effect is small when compared to the amount of monomer adsorbed by the polymer, particularly if the size and number of stopcocks in contact with the monomer are kept to a minimum.

TABLE 2

Effect of stepwise increase of pressure on the takeup of monomer by stopcock grease.

Pressure	Monomer adsorbed
(Torr)	(ml N.T.P.)
142.8	--
150.4	-0.02
157.4	-0.04
163.5	-0.02
169.7	+0.03
177.8	0.00
187.2	0.00
200.2	+0.01

3.2 The effect on the reaction of sudden pressure changes.

The apparatus described above was now used in a series of experiments to examine the effect of sudden pressure changes on the course of the adsorption of vinyl chloride on 4.4 grams of polyvinyl chloride at 42.6°C. To establish a pattern of normal behaviour, a series of uninterrupted runs at 42.6°C and different initial pressures, were performed. One such run is shown in Figure 23 in which amount adsorbed is plotted against time. Figure 24 shows the same run plotted as amount adsorbed against log time and Figure 25 shows three such runs.

Strictly speaking these runs are neither at constant volume nor constant pressure. There are small volume changes throughout the course of a run due to the movement of the mercury in the gas burette and the arms of the manometer as the pressure falls. These volume changes were taken into account when the amount adsorbed was calculated; the volume of the system being calibrated to a fixed mark on the manometer; the diameter of the tubing from which the manometer was constructed being known; the gas burette being read in the usual manner. The average volume change during the course of a run, from the first reading to the last, amounted to approximately 2% of the original volume. The pressure change over the same time interval being of the order of 5%.

The runs illustrated in Figures 23, 24 and 25 all have similar characteristics. There is a very rapid initial uptake of monomer followed by a slower process. If the run shown in Figures 23 and 24 is taken as an example it can be seen that for a total of 14.75 ml at N.T.P. adsorbed over 150 minutes, 12.66 ml or 85% of the total amount is taken up in the first minute of the reaction. The plot of amount adsorbed against log time is curved for the first ten minutes, the curvature being concave towards the log time axis. Thereafter the plot becomes almost linear for the rest

FIG. 23

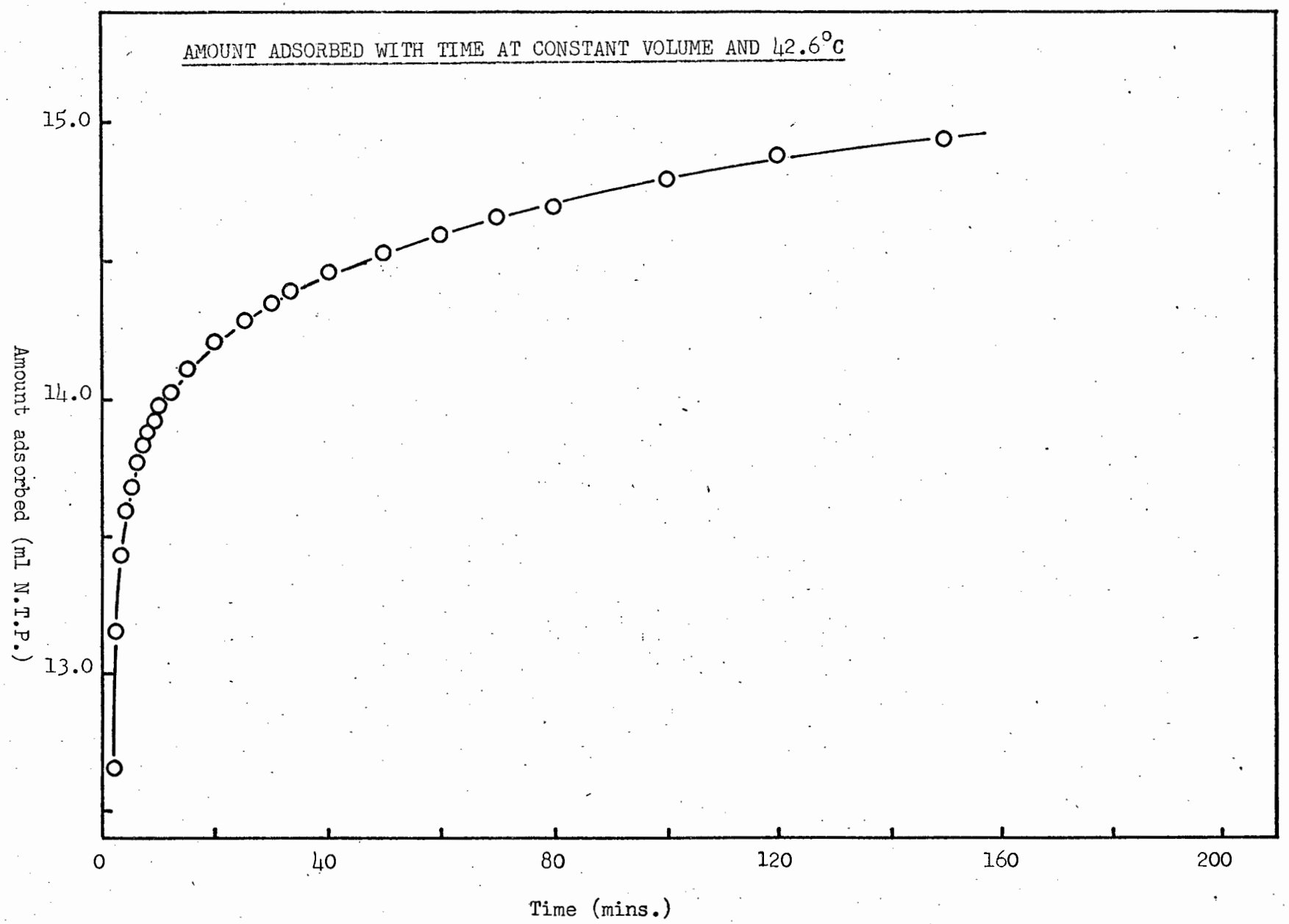

AMOUNT ADSORBED WITH TIME AT CONSTANT VOLUME AND 42.6°C
15.0
14.0
13.0
Amount adsorbed (ml N.T.P.)
0
40
80
120
160
200
Time (mins.)

FIG. 24

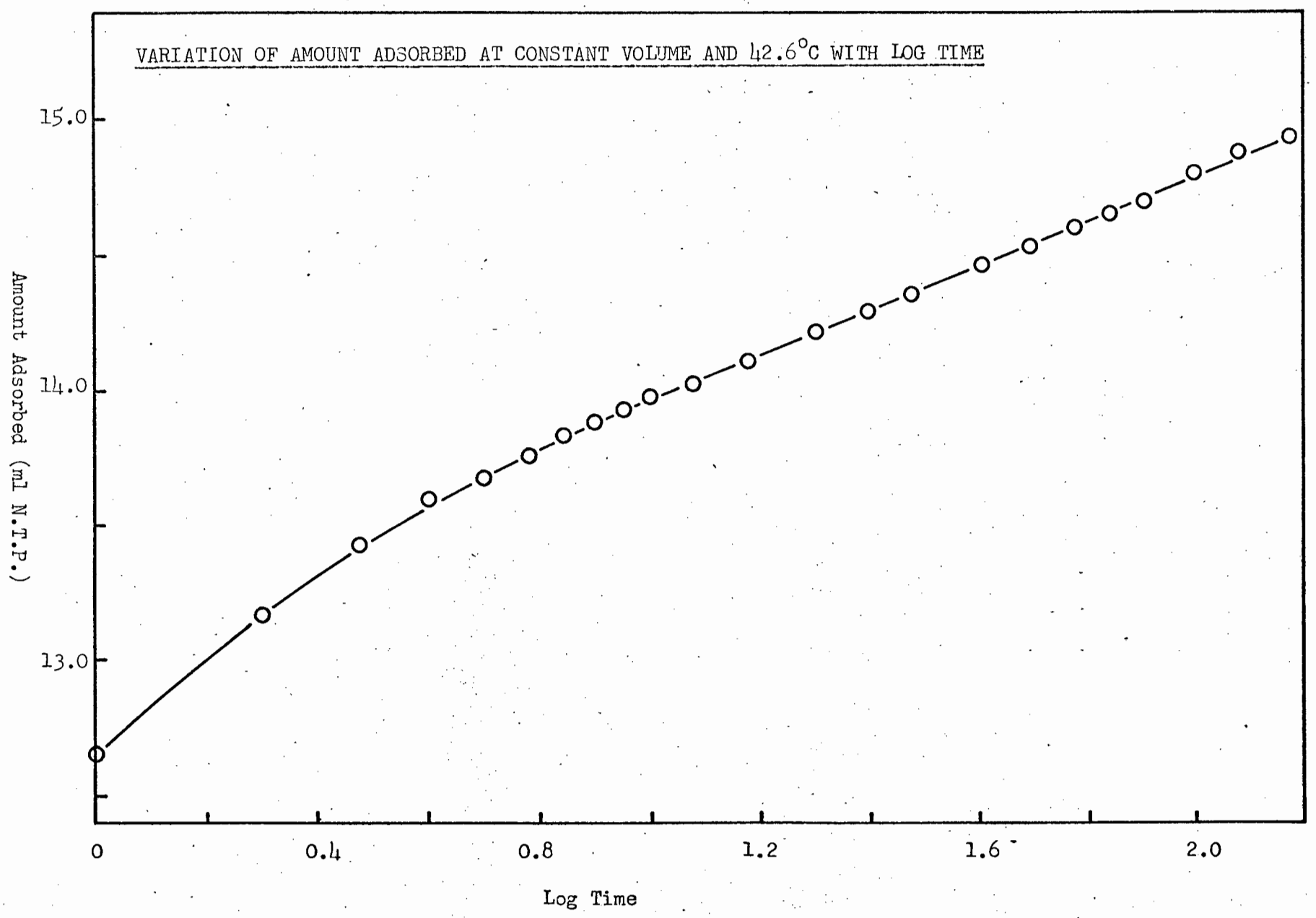
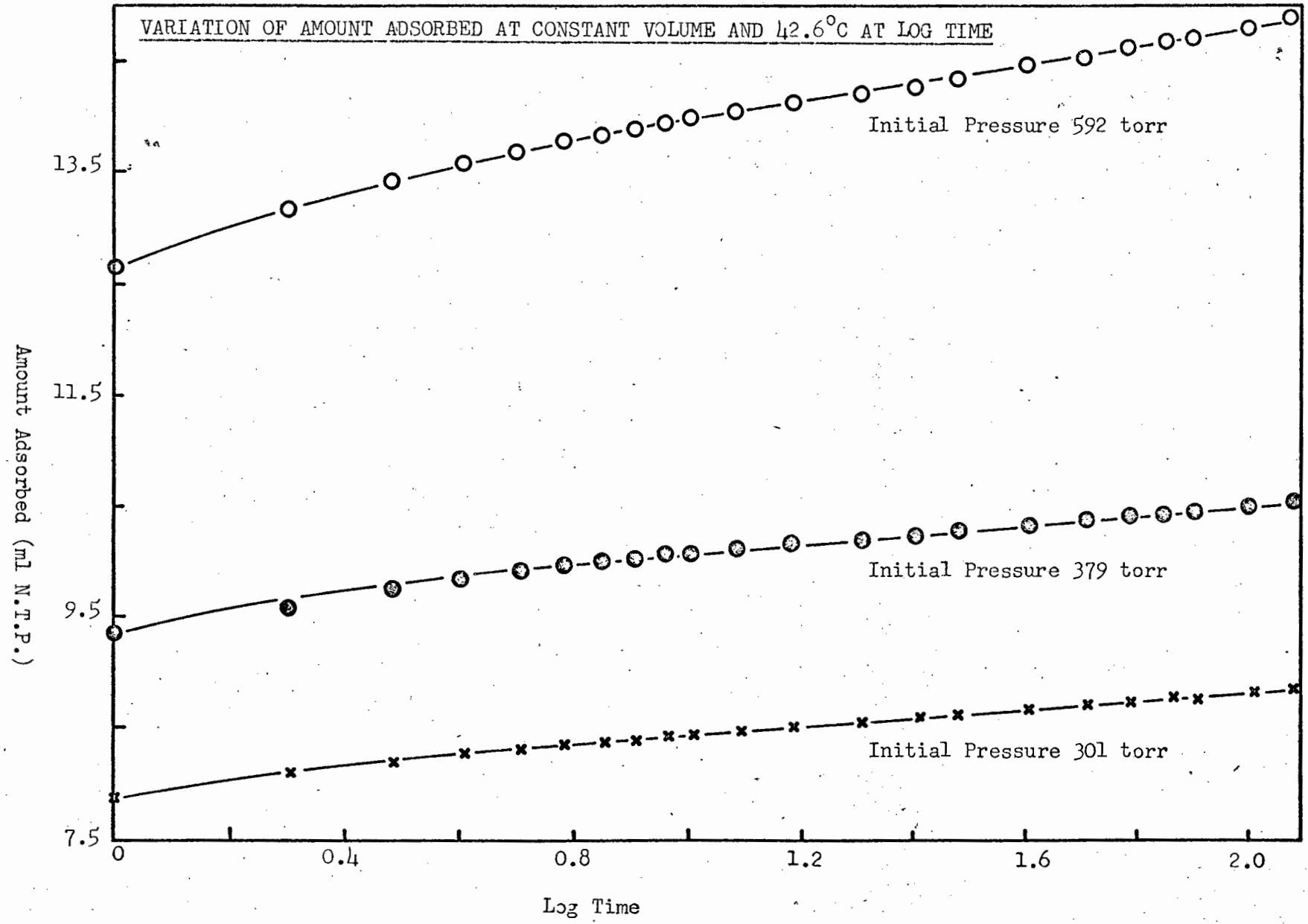

VARIATION OF AMOUNT ADSORBED AT CONSTANT VOLUME AND 42.6°C WITH LOG TIME
15.0
14.0
13.0
Amount Adsorbed (ml N.T.P.)
0
0.4
0.8
1.2
1.6
2.0
Log Time

FIG. 25


VARIATION OF AMOUNT ADSORBED AT CONSTANT VOLUME AND 42.6°C AT LOG TIME
Initial Pressure 592 torr
Initial Pressure 379 torr
Initial Pressure 301 torr
Amount Adsorbed (ml N.T.P.)
13.5
11.5
9.5
7.5
0
0.4
0.8
1.2
1.6
2.0
Log Time

of the period of measurement. The other runs shown in Figure 25 behaved similarly but there seemed to be a tendency for the slope of the linear region of the curve to decrease as the initial pressure decreased.

3.2.1 Sudden increase in pressure after ten minutes.

Figure 26 illustrates the effect of increasing the pressure during the course of a run. Ten minutes after the monomer had been allowed to come into contact with the polymer, the pressure in the system was increased by raising the level of the mercury in the gas burette. As Figure 26 shows there was an instantaneous increase in the amount adsorbed followed by the usual slow increase. It was interesting to note that initially Run 24 was at a slightly lower pressure than Run 25 but that after the pressure increase Run 24 was at the higher pressure and that the slope of the linear region following the break was smaller for Run 25 than for Run 24.

3.2.2 Sudden decrease in pressure after ten minutes.

Figure 27 illustrates the effect of decreasing the pressure during the course of a run. Ten minutes after the monomer had been allowed to come into contact with the polymer, the pressure in the system was reduced by lowering the level of the mercury in the gas burette. As can be seen from the figure there was a very rapid desorption followed by a slow readsorption.

3.2.3 Changes in pressure after a period greater than twenty hours.

Figure 28 illustrates the effect of allowing the reaction to proceed for approximately 24 hours (curve a). At the end of this period the pressure was increased and the course of the reaction at the higher pressure followed (curve b), zero time being taken as the moment at which

FIG. 26

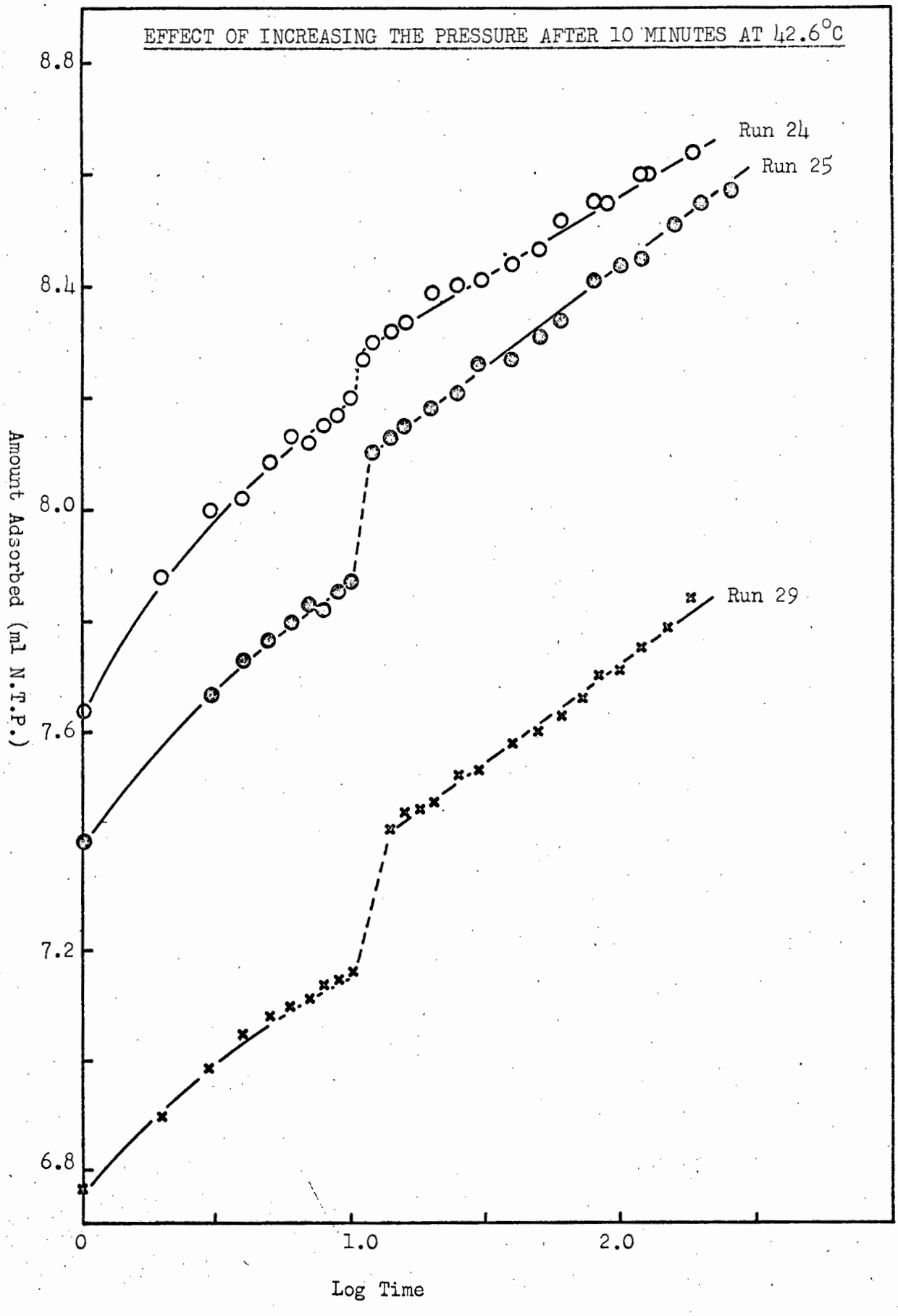
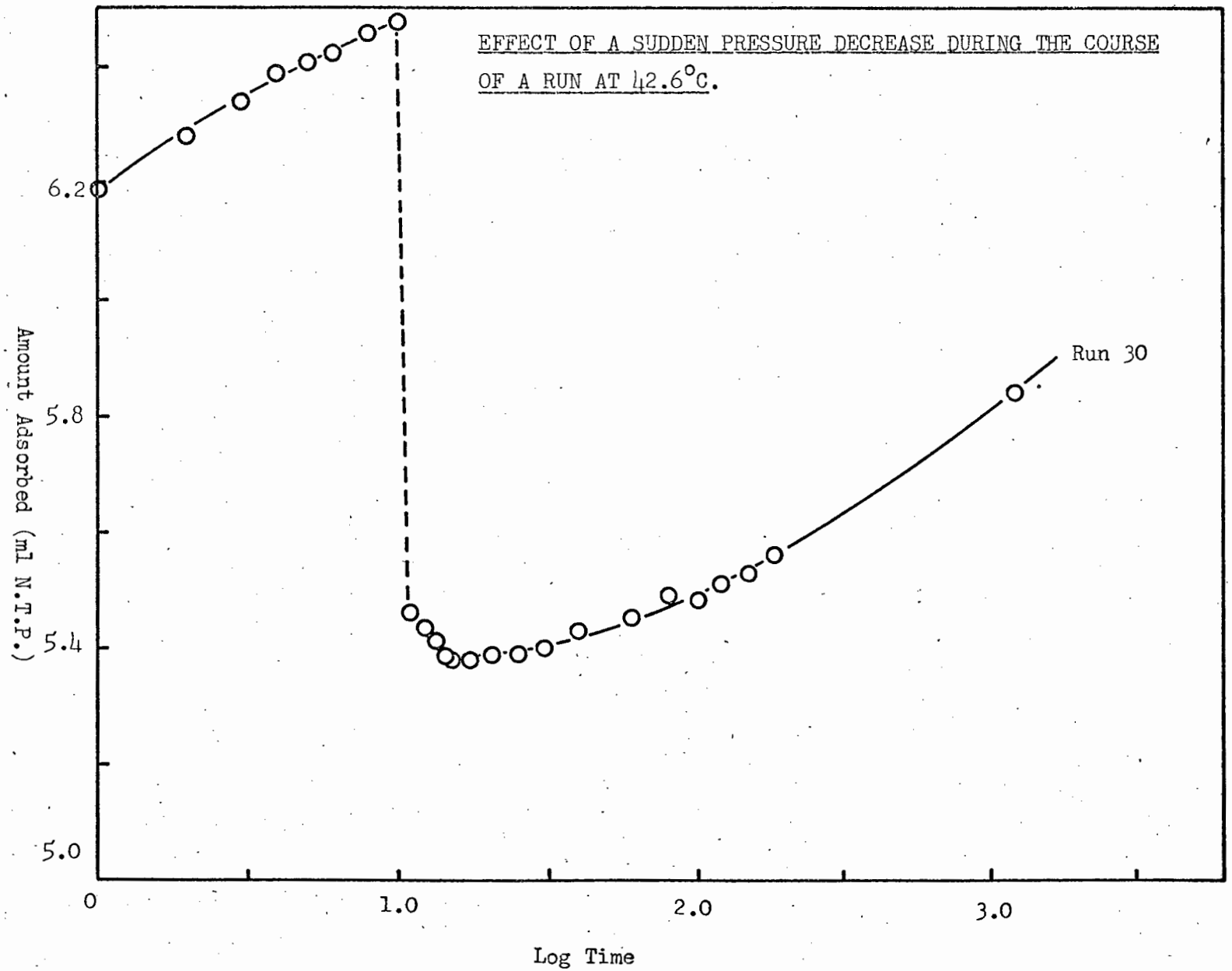

EFFECT OF INCREASING THE PRESSURE AFTER 10 MINUTES AT 42.6°C
Run 24
Run 25
Run 29
8.8
8.4
8.0
7.6
7.2
6.8
Amount Adsorbed (ml N.T.P.)
0
1.0
2.0
Log Time

FIG. 27


EFFECT OF A SUDDEN PRESSURE DECREASE DURING THE COURSE OF A RUN AT 42.6°C.
Run 30
Amount Adsorbed (ml N.T.P.)
6.2
5.8
5.4
5.0
0
1.0
2.0
3.0
Log Time

the pressure was increased. After a further 24 hours the pressure was decreased and the course of the reaction at the lower pressure followed (curve c), zero time being taken as the moment at which the pressure was lowered. The general shapes of curves a, b and c were later confirmed using a different apparatus which will be described in Section 3.3. The results obtained using this apparatus are shown in Figure 29. It must be noted that the results shown in Figure 29 represent very much larger pressure changes and longer time periods than do the results shown in Figure 28.

Figures 28 and 29 show that when monomer was left in contact with the polymer for a period such that the slow process proceeded for some time, then on increasing the pressure there was a rapid uptake of monomer followed again by a slow uptake. However, provided that the pressure increase was not too large, the amount of monomer taken up by the slow process was small enough to be practically neglected for the first twenty minutes or so after the pressure had been increased. Similarly reducing the pressure led to an initial rapid desorption followed by a very much slower desorption process. Also there was no readsorption.

It was thought, therefore, that the reversibility of the rapid uptake towards pressure could be tested by allowing monomer to remain in contact with polymer for a twenty hour period and then calculating the amount of monomer adsorbed. Thereafter the pressure in the system could be raised stepwise by raising the mercury in the gas burette and calculating the amount of monomer adsorbed immediately after each pressure increase. After the highest pressure had been attained the pressure could be decreased stepwise by lowering the mercury in the gas burette and calculating the amount of monomer remaining on the surface after each step. If the rapid uptake of monomer was reversible towards pressure and if the experiment was

FIG. 28

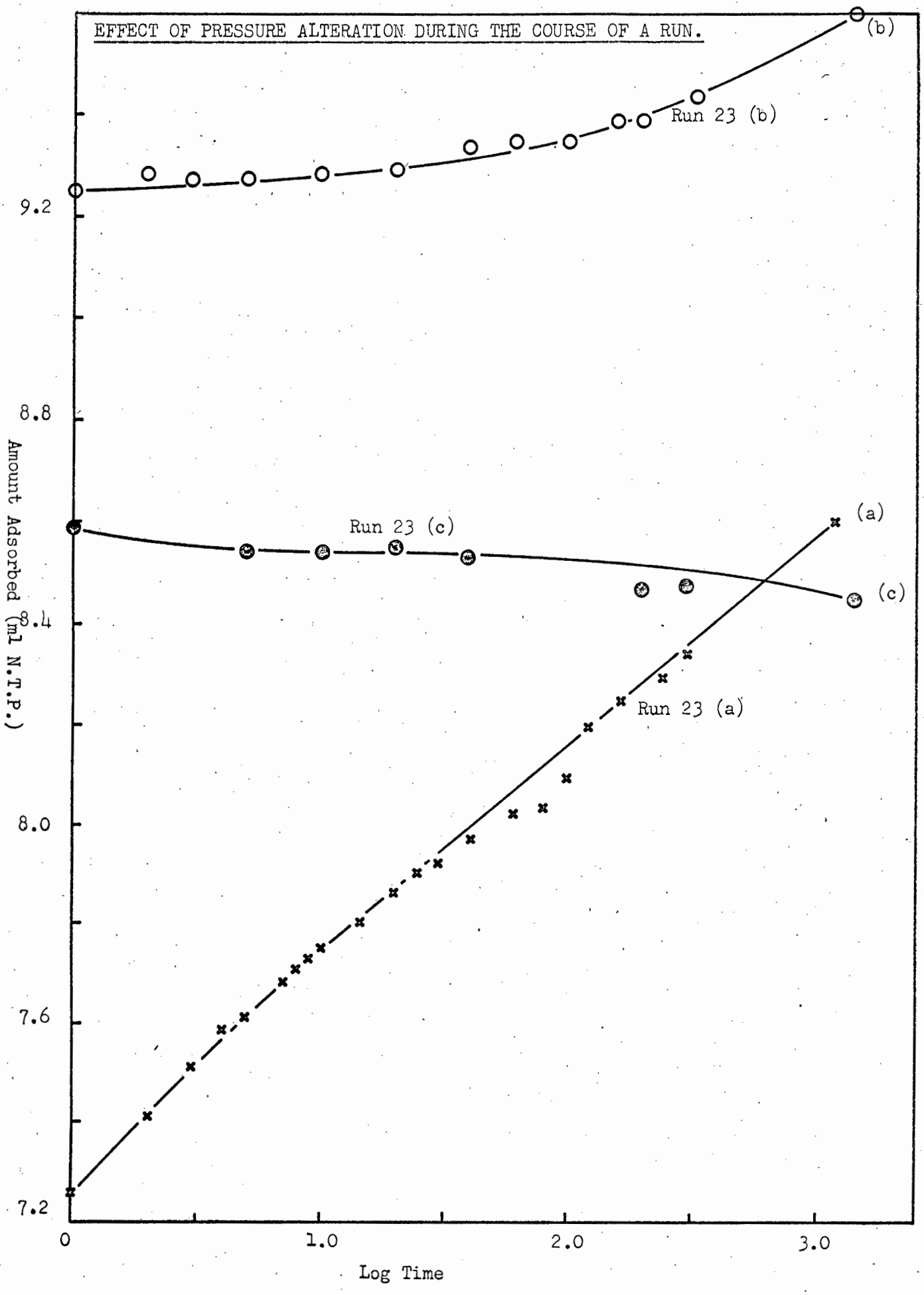
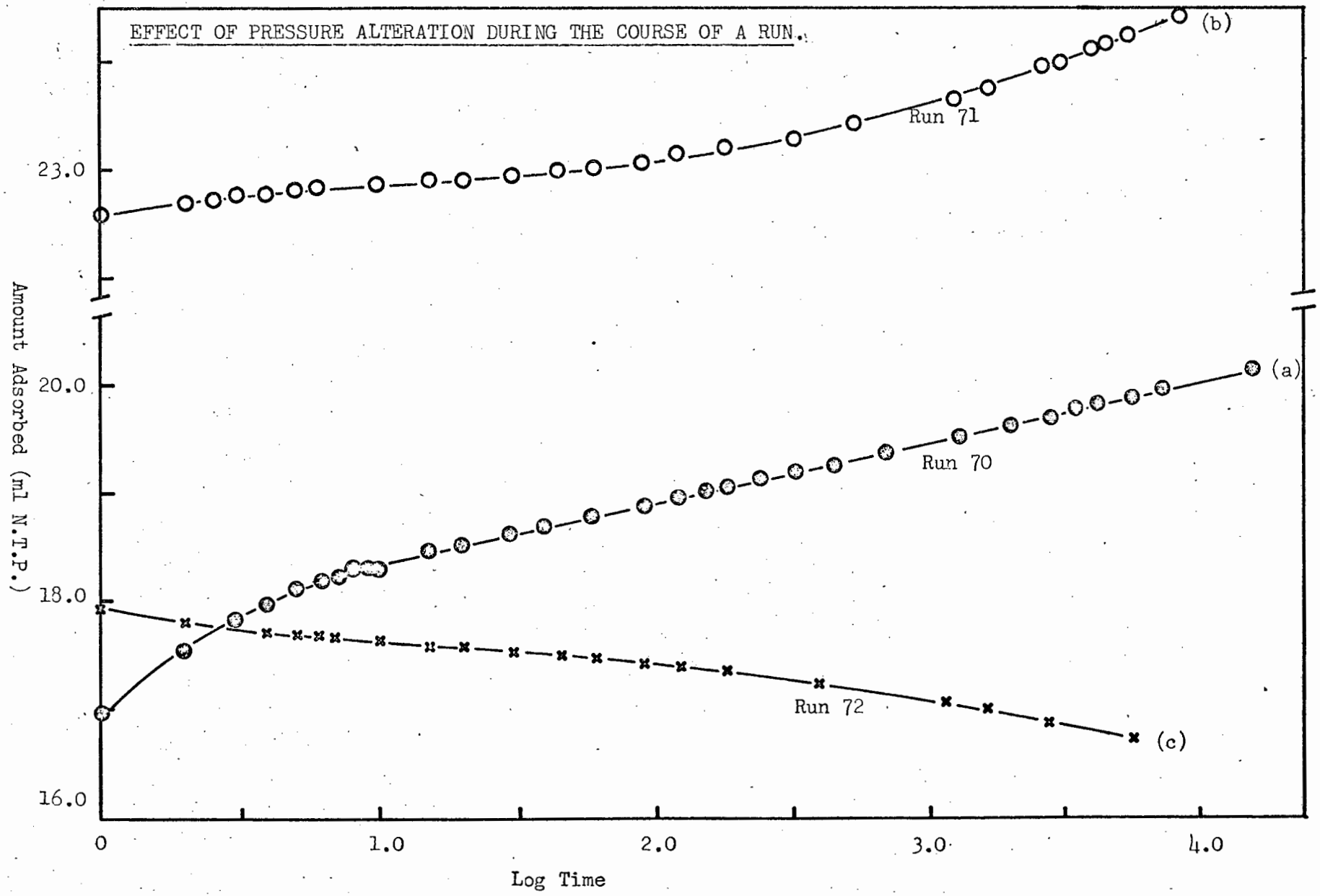

EFFECT OF PRESSURE ALTERATION DURING THE COURSE OF A RUN.
(b)
Run 23 (b)
9.2
8.8
Amount Adsorbed (ml N.T.P.)
Run 23 (c)
(a)
(c)
8.4
Run 23 (a)
8.0
7.6
7.2
0
1.0
2.0
3.0
Log Time

FIG. 29


EFFECT OF PRESSURE ALTERATION DURING THE COURSE OF A RUN.
Amount Adsorbed (ml N.T.P.)
23.0
20.0
18.0
16.0
0
1.0
2.0
3.0
4.0
Log Time
Run 71
(b)
Run 70
(a)
Run 72
(c)

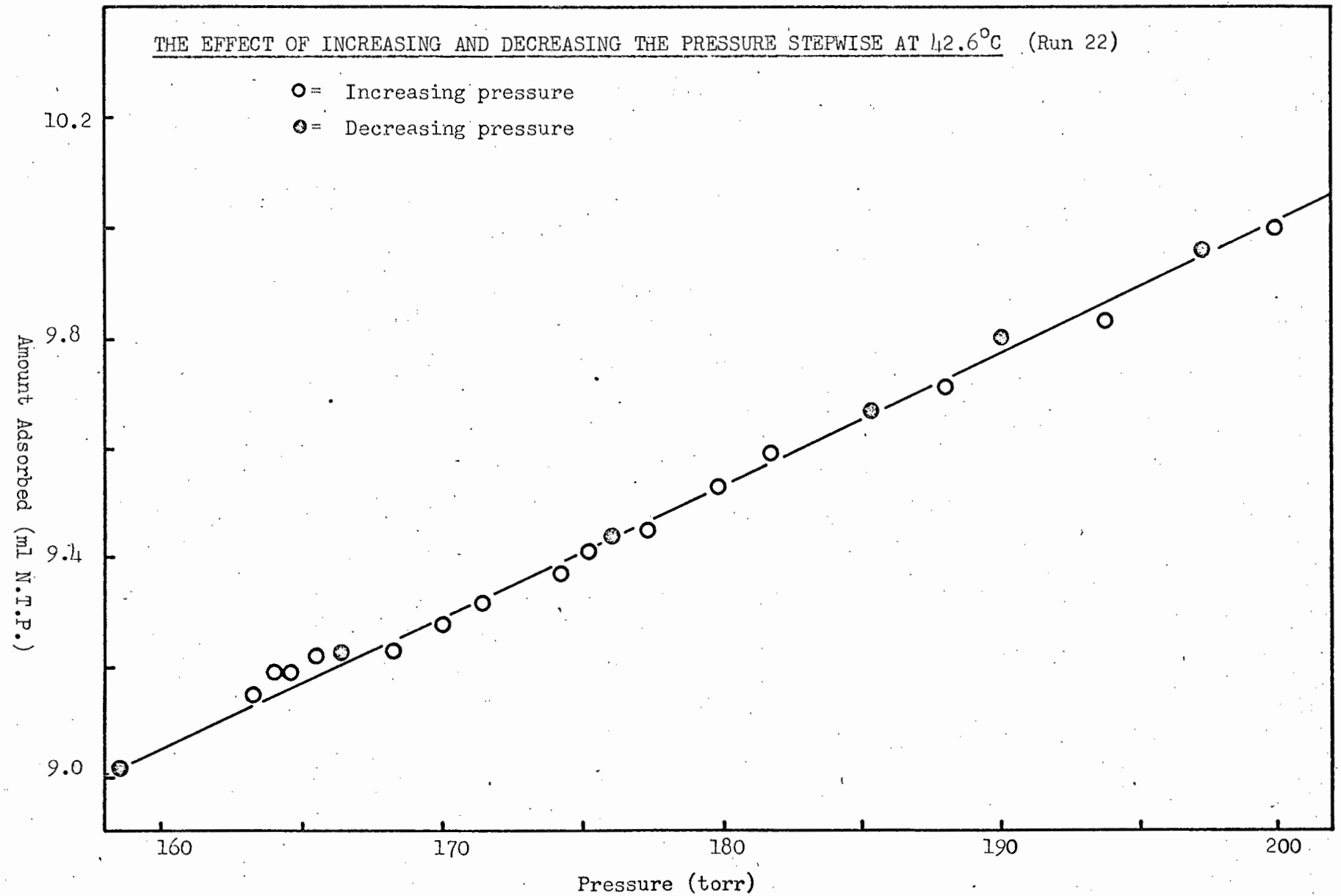
of short enough duration for the slow adsorption and desorption to be negligible, then the results for increasing and decreasing pressure should all lie on the same smooth curve.

The experiment was performed as outlined above, the duration of the experiment being of the order of fifteen minutes. The results plotted as amount adsorbed against pressure are shown in Figure 30.

This Figure shows that the adsorption and desorption points do lie on the same curve. The curve itself appears to be linear with a slope of 0.024 ml N.T.P/torr but this linearity could be misleading because of the narrow pressure range over which the measurements were made, i.e., if the rapidly adsorbed amounts obeyed some isotherm, for example the Freundlich isotherm, then over a short range of pressure this may well appear to be linear. Hence the measured slope of 0.024 ml N.T.P./torr can only be considered to be an estimate of the average slope of the isotherm obeyed by the rapid adsorption over the pressure range of the measurements. However, the fact that the adsorption and desorption points do lie on the same curve does indicate that the rapid amount adsorbed was probably reversible with respect to pressure.

An experiment, similar to the one described above, was later performed, using the apparatus referred to in Section 3.2.3 and described in Section 3.3, as a constant volume system. In this experiment monomer was allowed to remain in contact with the polymer for 72 hours. At the end of this period the pressure in the system was noted and the amount of monomer adsorbed calculated. The pressure was then increased by adding a further aliquot of monomer. Immediately after the addition of the extra monomer the pressure in the system was recorded and the amount of monomer adsorbed calculated. The system was then left to stand for 24 hours. At the end of this period the above sequence was repeated. This continued

FIG. 30


THE EFFECT OF INCREASING AND DECREASING THE PRESSURE STEPWISE AT 42.6°C (Run 22)
O = Increasing pressure
O = Decreasing pressure
10.2
9.8
9.4
9.0
Amount Adsorbed (ml N.T.P.)
160
170
180
190
200
Pressure (torr)

until the pressure in the system had been increased to 580 torr. For each addition of monomer the increase in the amount adsorbed was calculated and divided by the increase in pressure caused by the addition of the aliquot. The results for this experiment are tabulated in Table 3.

Table 3 shows that as the pressure in the system rises $\frac{\Delta s}{\Delta p}$ slowly decreases, bearing out what was said about the linearity of the plot shown in Figure 30. However, it can be seen from the table that the value of $\frac{\Delta s}{\Delta p}$ corresponds to the slope of the curve shown in Figure 30 over the same pressure range.

3.3 Effect of pressure on the rate of adsorption.

The runs described so far were all runs at constant volume, (Section 3.2), the pressure varying during the course of the run. The extent to which the pressure changed being dependent on the dead space volume of the system, the larger this volume and therefore the lower the precision of measurement, the smaller the pressure drop between initial and final reading. To examine the effect of pressure on the rate of reaction, it was therefore necessary to build an apparatus which could operate at constant pressure.

One practical consideration in designing such an apparatus was that the constant pressure device had to be relatively simple so that it could be built in the department. The constant pressure system described by Winter[80] did not meet this requirement, so it was decided to try the system described by Taylor and Strother.[58]

Basically the device shown in Figure 31 consisted of a gas burette A, over the mercury reservoir of which was built an electrolytic cell W, containing sodium hydroxide as electrolyte. When the pressure in the system fell electrical contact between the pair of tungsten wires C and C', sealed into one arm of the control manometer D, was broken because the

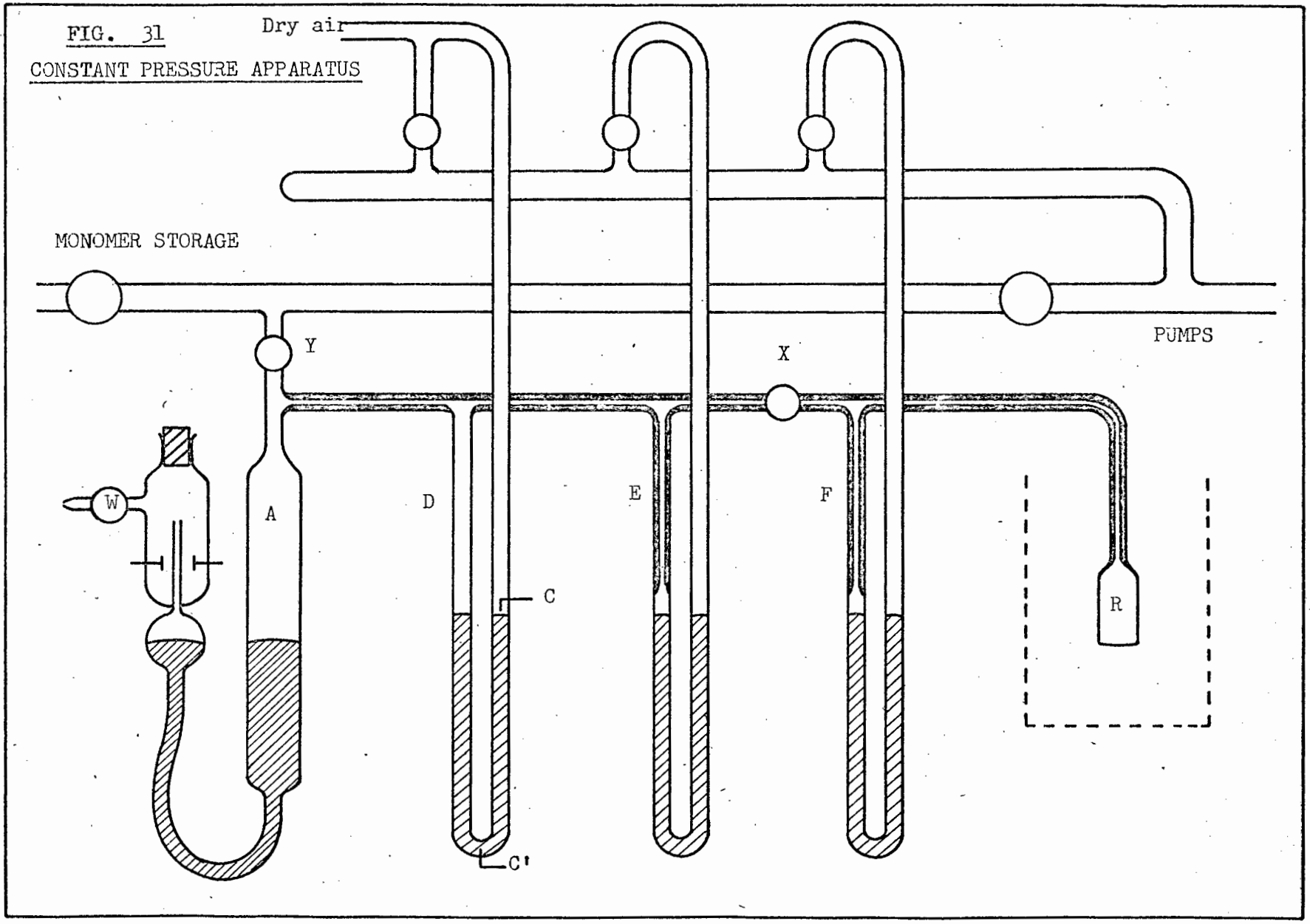
TABLE 3.

The immediate increase in amount adsorbed caused by changes in pressure at 42.6°C.

Initial Pressure (p_1)	Final Pressure (p_2)	Initial Amount adsorbed (s_1)	Final Amount adsorbed (s_2)	$\Delta s = s_2 - s_1$	$\Delta p = p_2 - p_1$	$\frac{\Delta s}{\Delta p}$
(torr)	(torr)	(ml N.T.P.)	(ml N.T.P.)	(ml N.T.P.)	(torr)	(ml/torr)
150.9	167.1	9.68	10.11	0.43	16.2	0.027
165.0	183.4	10.15	10.60	0.45	18.4	0.024
181.8	198.3	10.62	11.03	0.41	16.5	0.025
194.6	219.2	11.11	11.75	0.64	24.6	0.026
214.9	238.2	11.84	12.33	0.49	23.3	0.021
233.2	255.9	12.45	12.95	0.50	22.7	0.022
251.3	276.1	13.05	13.48	0.43	24.8	0.017
268.9	295.4	13.67	14.20	0.53	26.5	0.020
291.0	314.9	14.31	14.74	0.43	23.9	0.018
309.5	337.5	14.89	15.42	0.53	28.0	0.019
332.8	351.1	15.54	15.84	0.30	18.3	0.016
346.7	383.3	15.96	16.60	0.64	36.6	0.017
376.9	403.1	16.78	17.22	0.44	26.2	0.017
393.8	421.1	17.49	17.93	0.44	27.3	0.016
415.9	450.8	18.07	18.59	0.52	34.9	0.015
443.7	480.0	18.80	19.39	0.59	36.3	0.016
473.1	506.9	19.60	20.12	0.52	33.8	0.015
500.0	558.1	20.35	21.28	0.93	58.1	0.016
549.3	582.0	21.57	22.08	0.51	32.7	0.016

FIG. 31

CONSTANT PRESSURE APPARATUS



mercury in the arm fell away from the upper contact. This operated a relay which caused the electrolytic cell to be switched on. The gases generated in the cell forced the mercury up the gas burette thus reducing the volume of the system and hence increasing the pressure. If the pressure on the contact side of the control manometer D was kept constant, the pressure in the system would remain constant.

This simple device worked well provided that the reaction was not too fast. Using it, it was found possible to maintain the pressure in the system constant to within ± 1 torr.

The rest of the apparatus, as shown in Figure 31, consisted of two mercury manometers E and F, one on each side of the stopcock X, X being the stopcock separating the thermostatted reaction vessel R from the rest of the apparatus. To keep the volume of the system small, capillary tubing was used wherever possible.

The volume of the dead space between stopcocks Y and X to a fixed mark on the manometer E was determined by means of the gas burette A using dry nitrogen. The diameter of the tubing from which manometers E and F were constructed was known, so that the volume of the manometer to the fixed mark could be calculated for any given pressure. During the calibration it was ensured that the mercury level in the control manometer D always remained at the height of the upper contact C. The volume of the region determined in this fashion was found to be 37.71 ml ± 0.14 ml, at the 95% confidence limits.

In a similar fashion the volume of the region beyond stopcock X to a fixed mark on the manometer F with the reaction vessel at the temperature at which the run was to be performed was determined. With the reaction vessel at 42.6°C this section had a volume such that 10 torr pressure was equivalent to 0.1604 ml at N.T.P. ± 6×10^{-4} ml at the 95%

confidence limits.

The procedure for operating at constant pressure was as follows: With stopcock X closed monomer was let into the gas burette system via stopcock Y until the required pressure, preset on the control manometer D, was attained. After the section had been filled, the amount of monomer present could be calculated from the pressure recorded on manometer E, the reading of the gas burette, the known dead volume of the system, the temperature of the gas burette and room temperature. The pressure to which this section was filled with monomer was always above that required for the run, this being done to prevent the gas burette being overrun due to expansion and the large initial uptake. After the section had been filled and the amount of monomer calculated the pressure on the control side of manometer D was reduced to the pressure desired for the run. The run was started by opening stopcock X which was then left open for the rest of the run. The course of the reaction was followed by means of the changing volumes recorded on the gas burette A. At the beginning of a run it was usually necessary to make some manual adjustment of the height of the mercury reservoir of the gas burette.

Measurements at constant volume were carried out as follows: The gas burette section, with stopcock X closed, was filled as before and the amount of monomer filling it calculated. Stopcock X was then opened so that monomer could come into contact with the polymer and then reclosed. The amount of monomer remaining in the gas burette section could be calculated and hence the amount of monomer allowed into the reaction vessel could be calculated. The course of the reaction could then be followed by means of the pressure recorded on manometer F.

3.4 Measurements at constant pressure.

In all twenty uninterrupted runs at constant pressure and 42.6°C were performed. Figure 32A illustrates some of these runs plotted

as amount adsopbed against log time. Figure 32B shows one of these runs plotted on a larger scale. Figures 32A and 32B show that these runs exhibited the now familiar pattern, i.e., a very fast initial uptake of monomer followed by a slower process. The curves are qualitatively all very similar and are very similar to those obtained in earlier runs at constant volume. In all of them for the first ten minutes or so of the reaction, the curve is concave towards the log time axis, thereafter the curve becomes apparently linear over the remainderof the period of measurement, the slope of the linear region tending to decrease with decreasing pressure.

In the linear region of the curves the Elovich equation, in the form $\frac{dv}{d\tau} = ae^{-\alpha v}$ could be obeyed. The integrated form of this equation being:

$$v = \frac{2.3}{\alpha} \log \left[\tau + \tau_o\right] - \frac{2.3}{\alpha} \log \tau_o$$

where $\tau_o = \frac{1}{\alpha a}$ a = initial rate of the reaction v = the amount adsorbed by the process which obeys this rate law at a time τ since the commencement of the process.

It is clear, however, that over the first ten minutes or so of the process, the above equation cannot apply alone, i.e. if $\tau = t$, (t being the actual time which has elapsed since the monomer was allowed to come into contact with the polymer), then because the curve in this region is concave towards the log t axis it can only be linearised by τ_o being negative, which has no physical significance. It follows therefore that if a process was occurring which obeyed the Elovich equation then a second process, which does not obey this rate law, must also have been occurring in the first ten minutes or so of the adsorption.

FIG. 32A

VARIATION OF AMOUNT ADSORBED AT CONSTANT PRESSURE AND 42.6°C WITH LOG TIME.

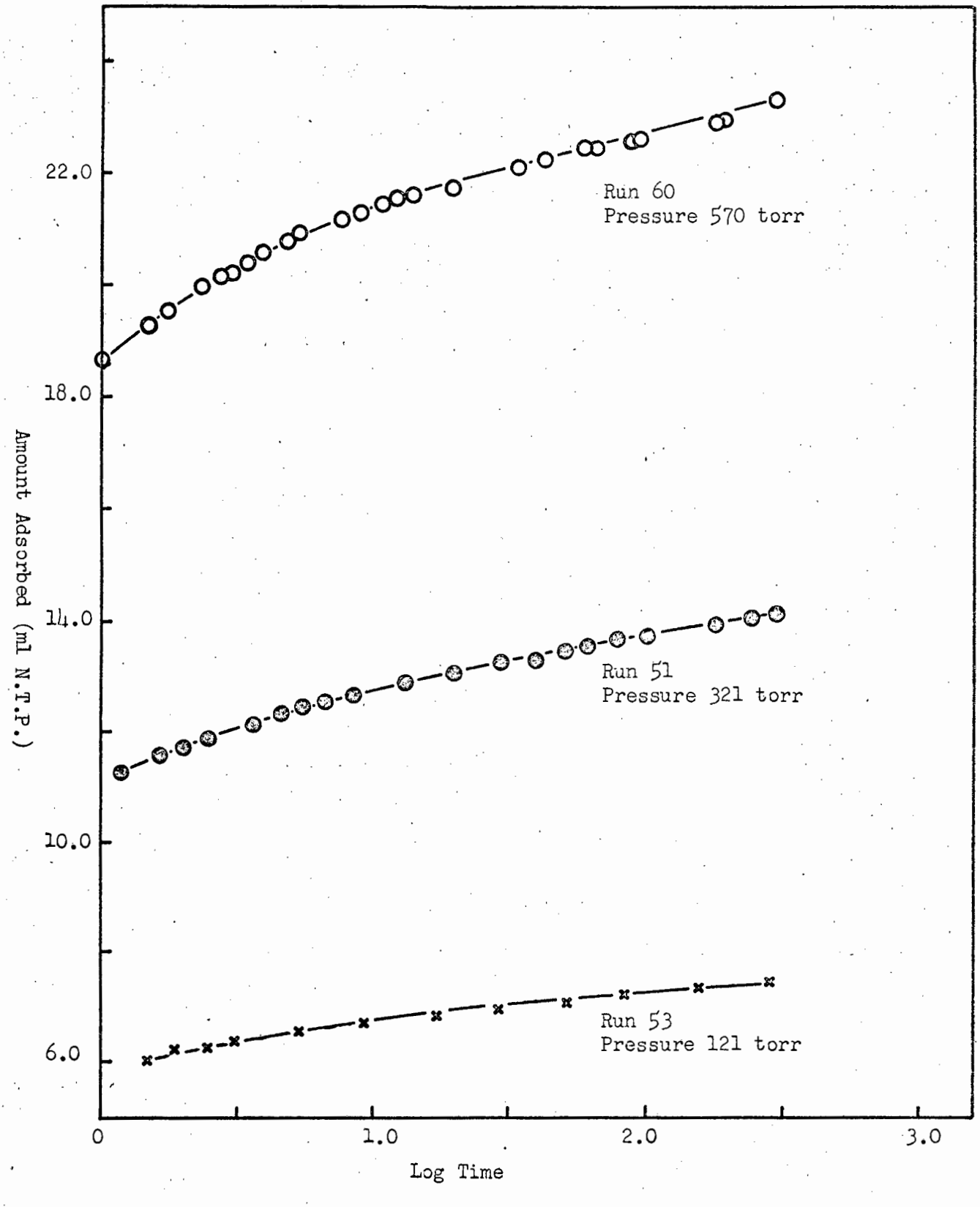
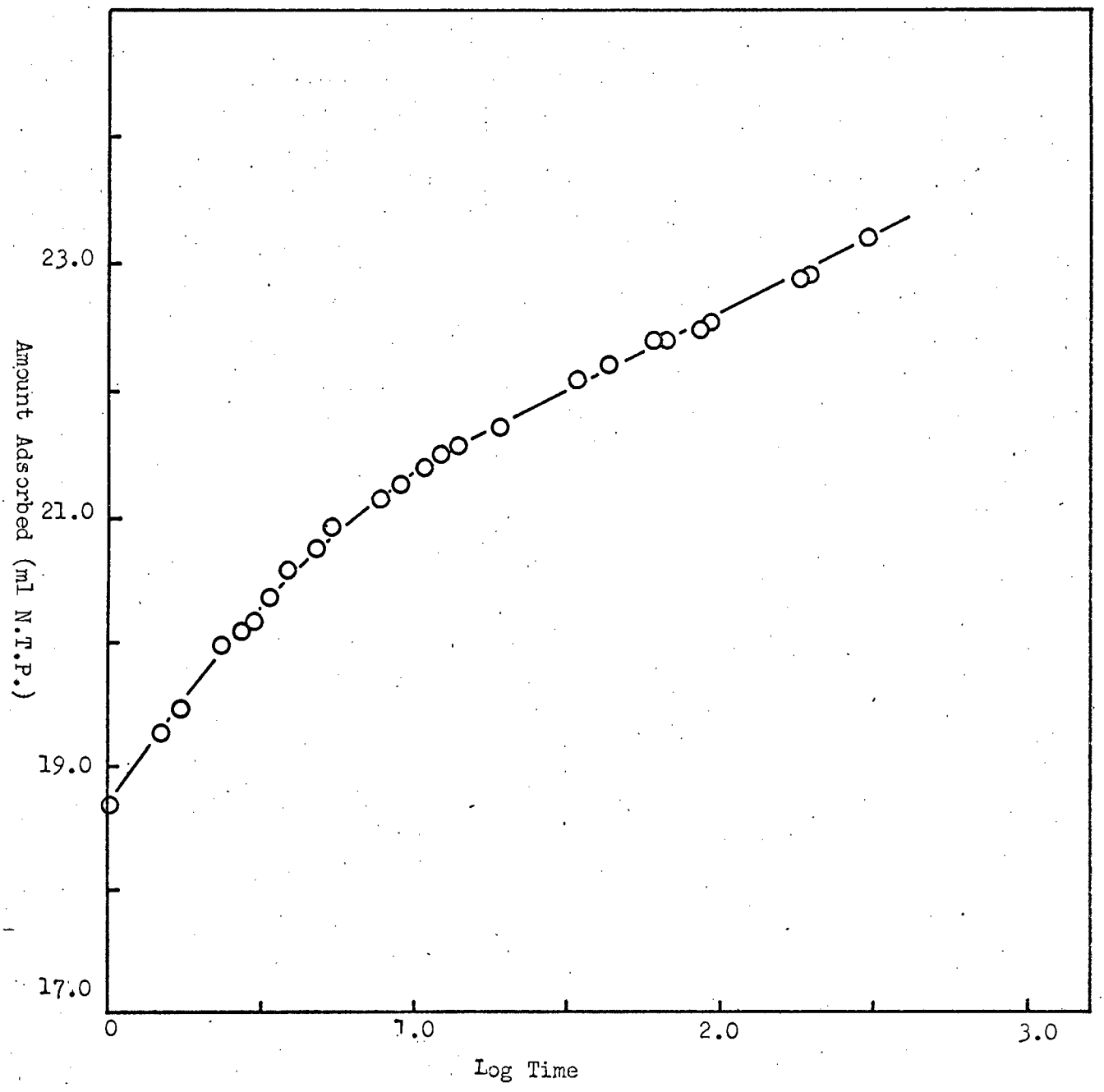


FIG. 32B

RUN 60 AT CONSTANT PRESSURE AND 42.6°C



3.5 Measurements at constant volume.

A series of runs at constant volume and varying initial pressures at 25°C and 42.6°C were performed and some of these are shown in Figure 33A and Figure 33B.

3.6 Effect of ambient pressure on the rate of the slow process.

In section 3.4 where the results obtained for runs done under constant pressure conditions were shown, it was observed that beyond ten minutes the plots of amount adsorbed against log time appeared to be linear. It was suggested that in this region a rate equation of the Elovich type could apply. It was also observed that as the pressure under which the runs were done decreased, so the slope of the log plots decreased. This decrease in slope with decreasing pressure suggested that if the Elovich equation applied then "α" in the exponential term of the equation must decrease with increasing pressure.

Generally it has been found that when the Elovich equation was applicable "α" was insensitive to the ambient pressure but showed some slight dependence on the initial pressure of the system.[81,82,62,65]

To test whether the observed changes in the slope of the log t plots for the vinyl chloride system were due to changes in the ambient pressure, the experiments described in sections 3.6.1 and 3.6.2 below were performed. The argument on which these experiments were based was that; if the rate of adsorption was dependent on the ambient pressure, then alteration of the rate at which the ambient pressure was changing, would result in a change of slope in the s - log t plot at the point at which the conditions were altered. Alteration in the rate of change of the ambient pressure could be brought about in two ways:

(i) by changing from conditions of constant pressure to those of constant volume.

FIG. 33A

RUNS AT CONSTANT VOLUME AND 25°C

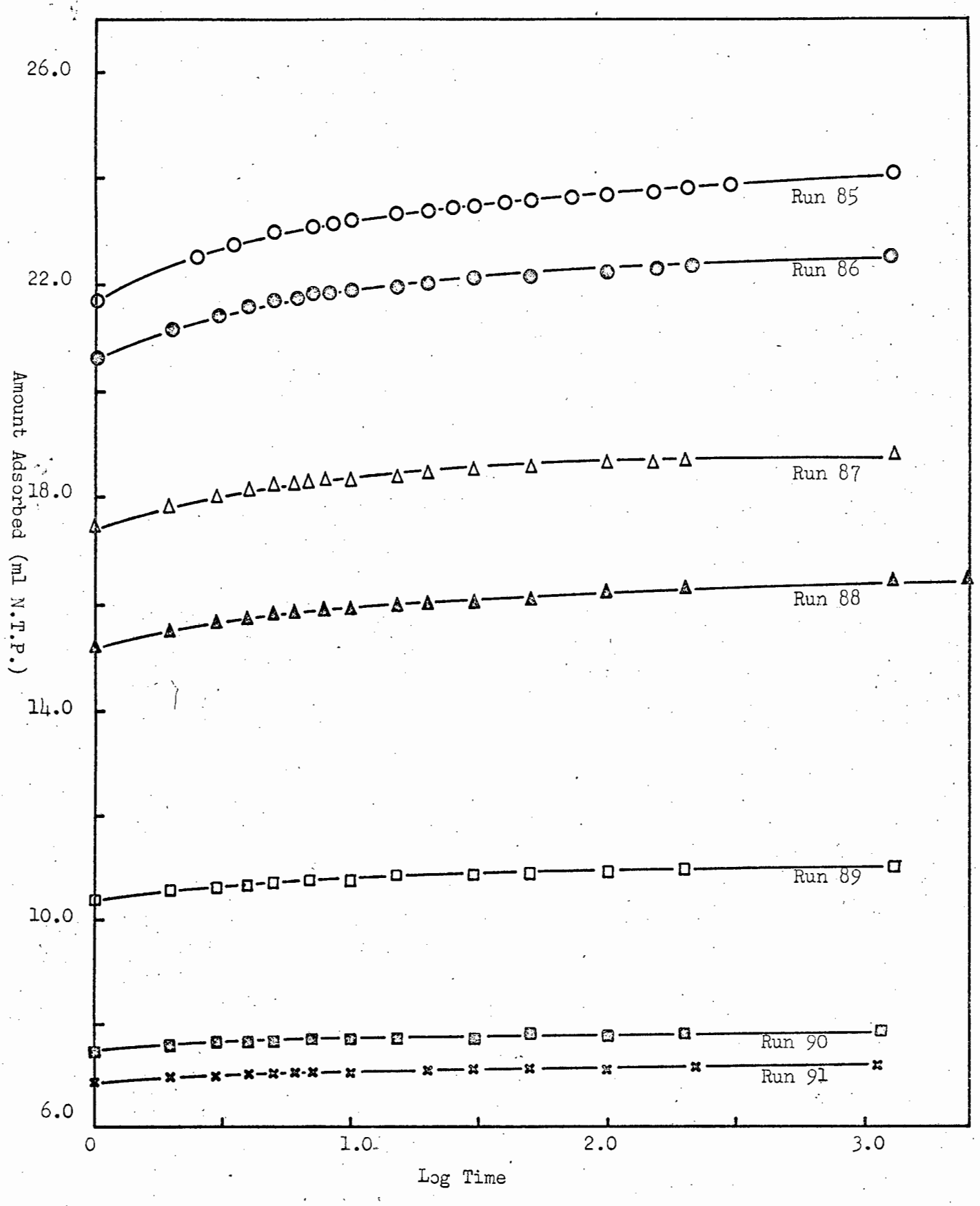
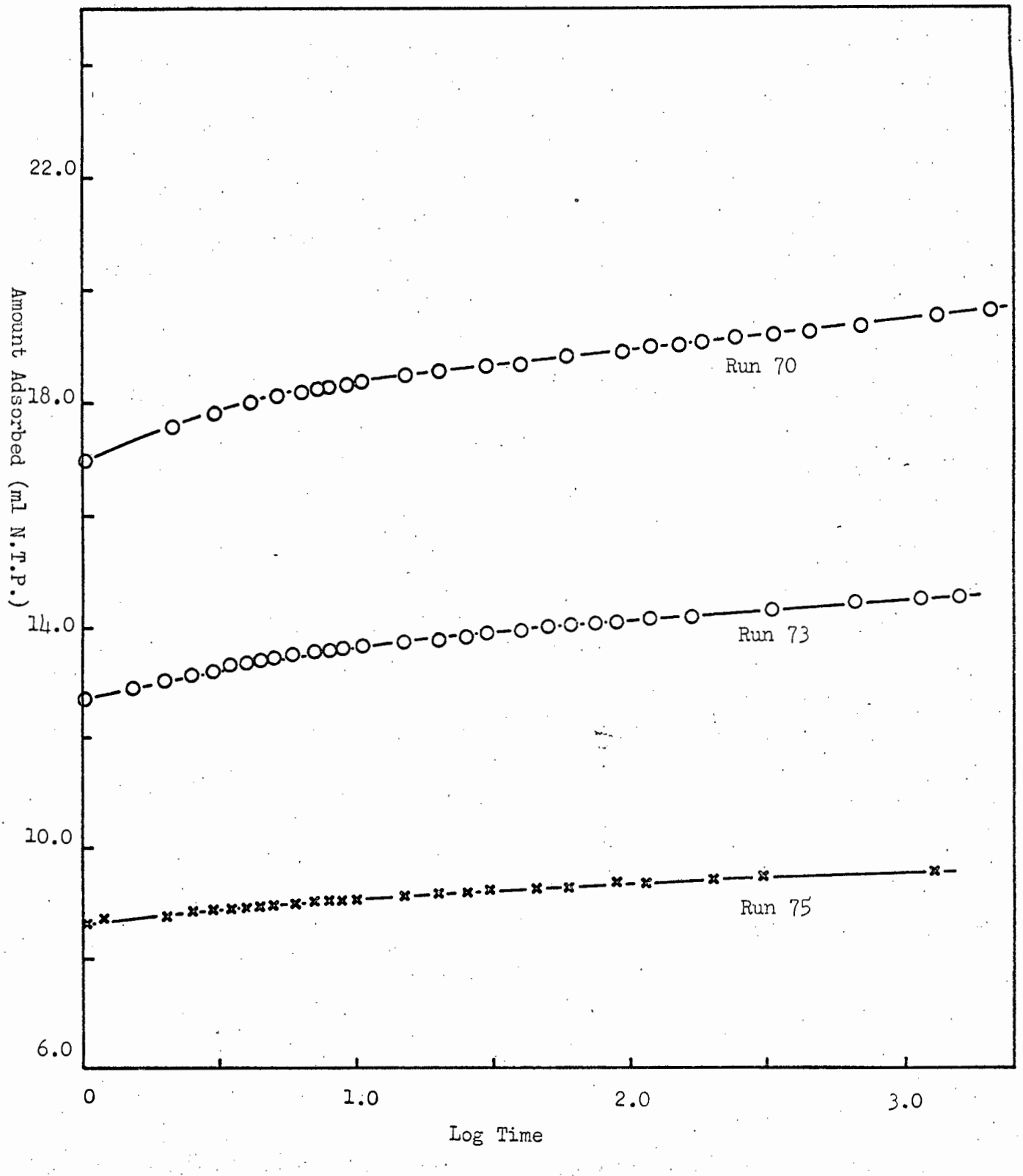


FIG. 33B

RUNS AT CONSTANT VOLUME AND 42.6°C



(ii) by reducing the volume of the system during the course of a run at constant volume.

In both cases (i) and (ii) above it would be expected that if the rate of adsorption was dependent on the ambient pressure, then the slope of the s - log t plot would be smaller after the change in the conditions than before. Figures 34 and 36 show that this was the case.

3.6.1 Conversion from constant pressure conditions to constant volume conditions during the course of a run.

In this series of experiments at 25°C monomer was adsorbed on the polymer at constant pressure for 71 minutes, the course of the reaction being followed in the usual manner. After 71 minutes had elapsed the system was converted to constant volume by closing stopcock X, the course of the reaction for the rest of the run being followed by means of manometer F. The results obtained for a typical run are shown in Figure 34.

3.6.2 The effect of reducing the volume of the system without altering the pressure during the course of a run at constant volume.

For this experiment the apparatus had to be modified in the following manner. A bulb P of approximately 25 ml capacity was sealed on to the apparatus on the reaction vessel side of stopcock X. This bulb could be isolated from the adsorption vessel and the rest of the apparatus by means of the three-way stopcock Z. The modified apparatus beyond stopcock X is shown in Figure 35.

After calibration, the following experiment was performed. The system was degassed and then the adsorption vessel was isolated from the rest of the system by means of stopcock Z. The system was filled with a known amount of monomer via stopcock X and stopcock X was closed. Stopcock Z was then rotated so as to include the adsorption vessel in the

FIG. 34

CONVERSION FROM CONDITIONS OF CONSTANT PRESSURE TO THOSE OF CONSTANT VOLUME AT 25°C. (RUN 77).

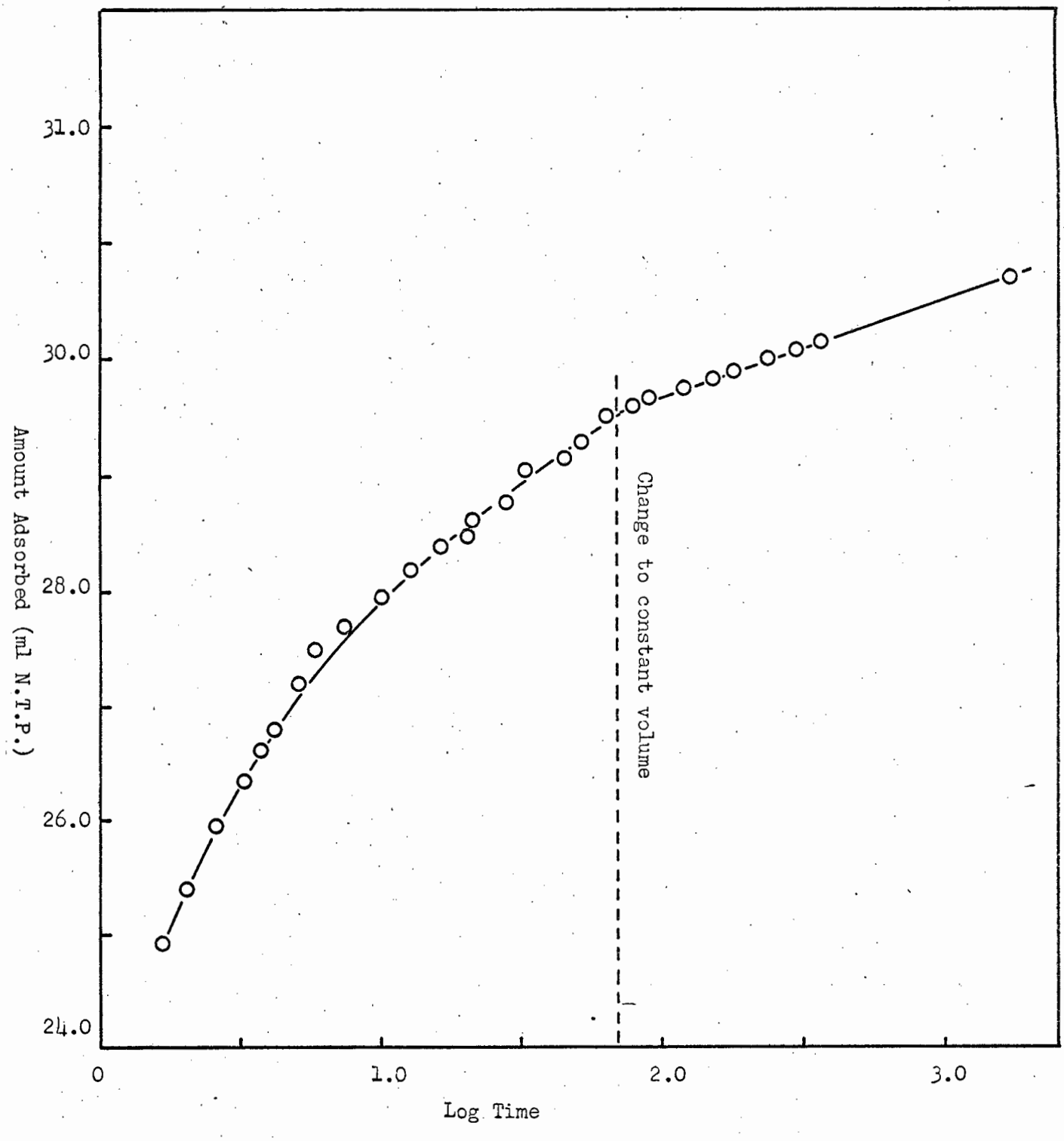


FIG. 35

ADDITION OF EXTRA VOLUME BULB P TO THE APPARATUS

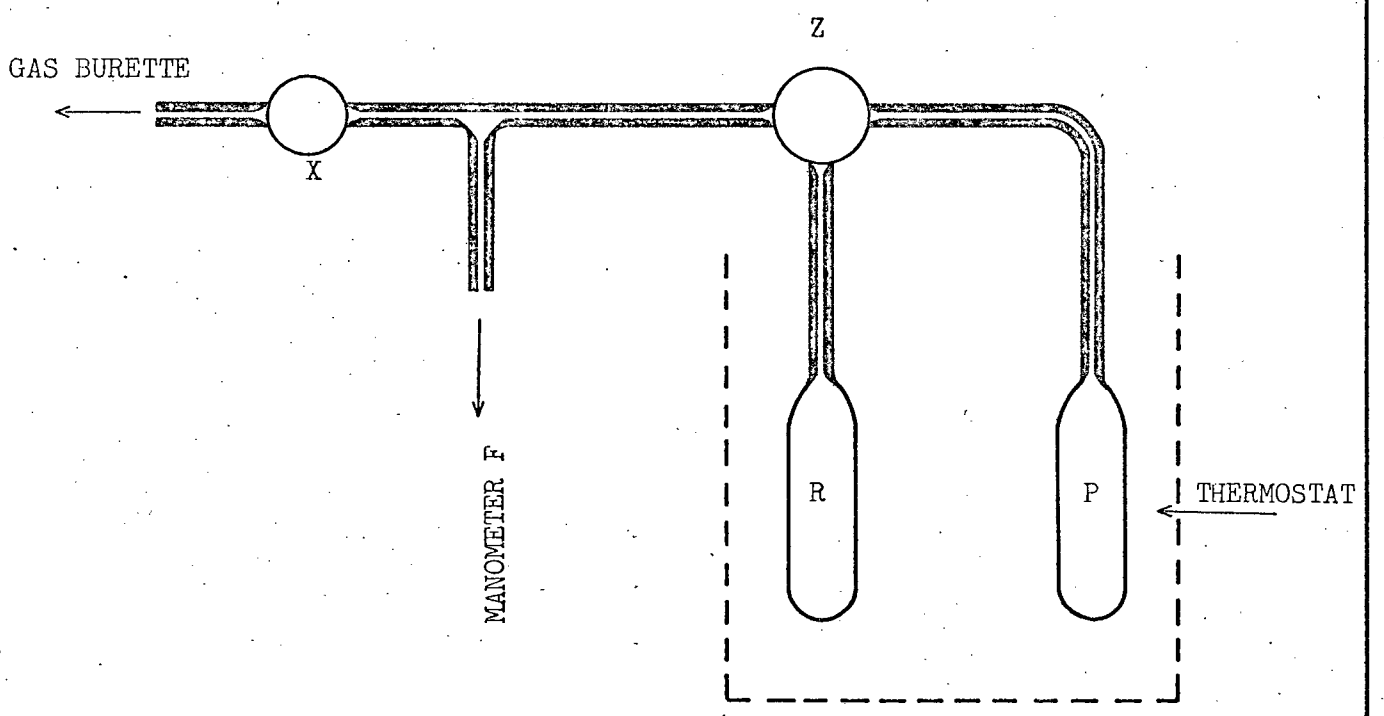
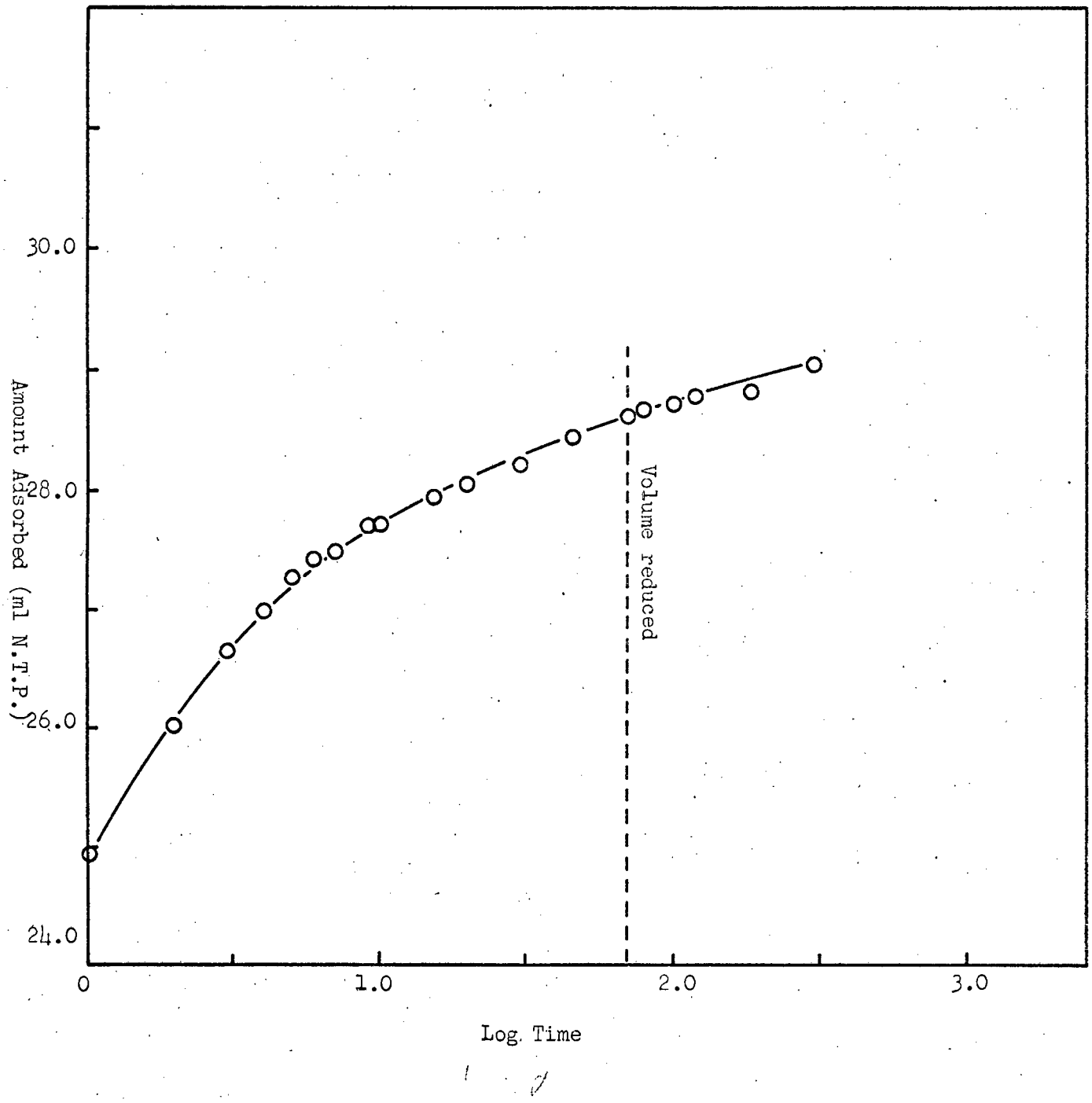


FIG. 36

THE EFFECT OF CHANGING THE VOLUME OF THE SYSTEM DURING THE COURSE OF THE RUN AT 25°C. (RUN 80).



system and the course of the run at constant volume followed by means of manometer F. After approximately 70 minutes had elapsed the extra bulb P was isolated from the system by rotating Z and the course of the reaction, under these conditions, followed for a further 230 minutes.

Only one such experiment at 25°C was performed, the results for which are shown in Figure 36.

3.7 The effect of altering the pressure during the course of a run at times greater than ten minutes.

For these experiments the apparatus, as shown in Figure 31, was used. The procedure adopted was as follows: A conventional rate run at constant pressure and 42.6°C was started and allowed to proceed for 47 minutes in one case and 116 minutes in another. After the given period of time had elapsed the pressure in the system was raised by raising the mercury in the gas burette A and kept constant at this new value for the rest of the run. The results, which are similar to those shown earlier for a constant volume system, are shown in Figure 37.

3.8 Adsorption isotherms.

Isotherms were measured at two temperatures, viz., 42.0°C and 25.0°C using the apparatus of Figure 31 as a constant volume system. The procedure adopted was as follows: The sample was degassed and a small measured aliquot of monomer was allowed tc come into contact with the polymer and remain in contact for 48 hours. After this period of time had elapsed, the amount of monomer adsorbed was calculated and a second aliquot added without any intermediate pumping. This aliquot was also allowed to remain in contact with the polymer for 48 hours. This procedure was repeated with further aliquots. The two isotherms obtained are shown in Figure 38.

FIG. 37

THE EFFECT OF SUDDEN PRESSURE CHANGES ON THE COURSE OF THE ADSORPTION AT 42.6°C. (RUNS 61 AND 62)

O = Pressure changed after 116 minutes (Run 61)

⊙ = Pressure changed after 47 minutes (Run 62)

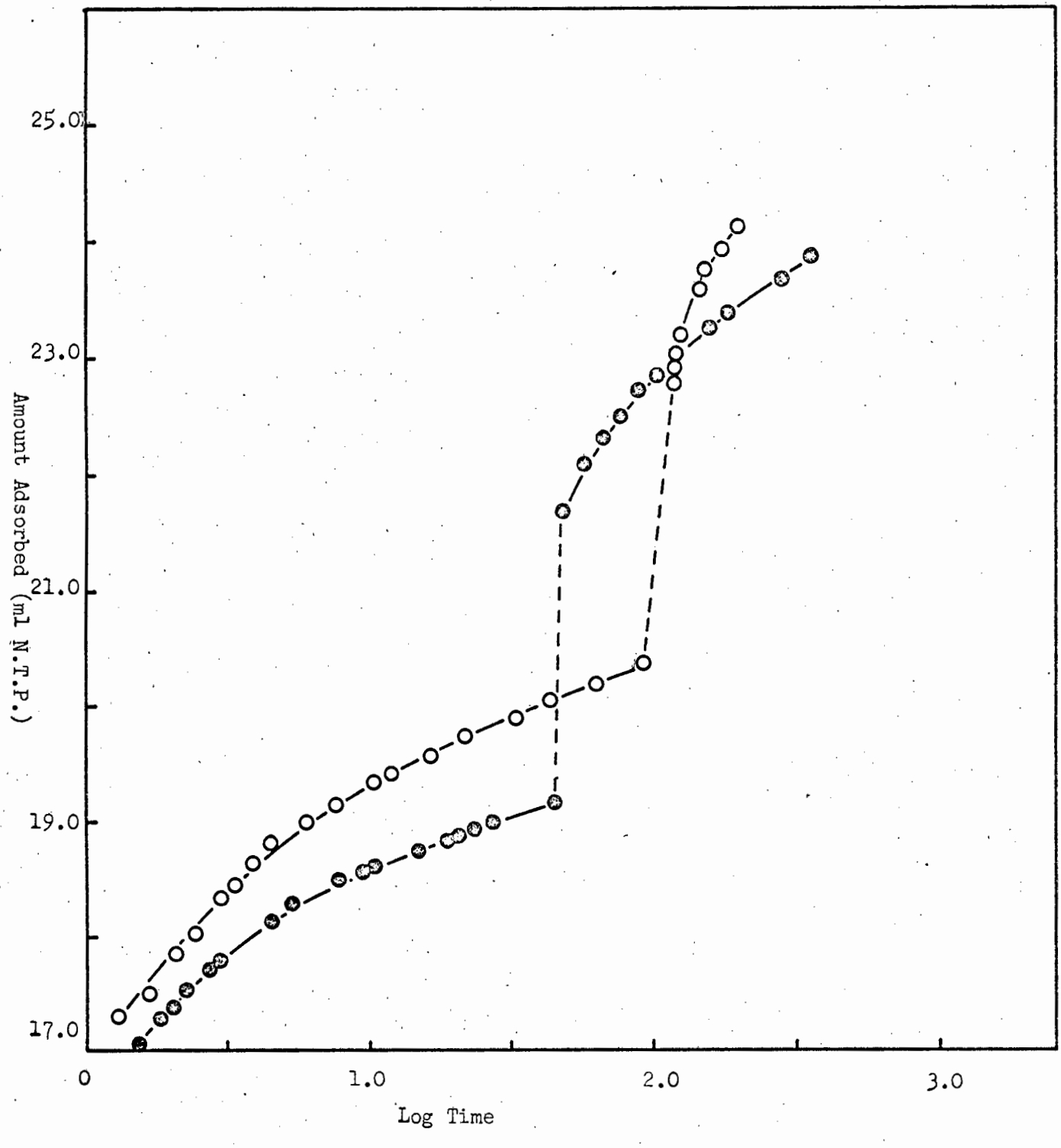
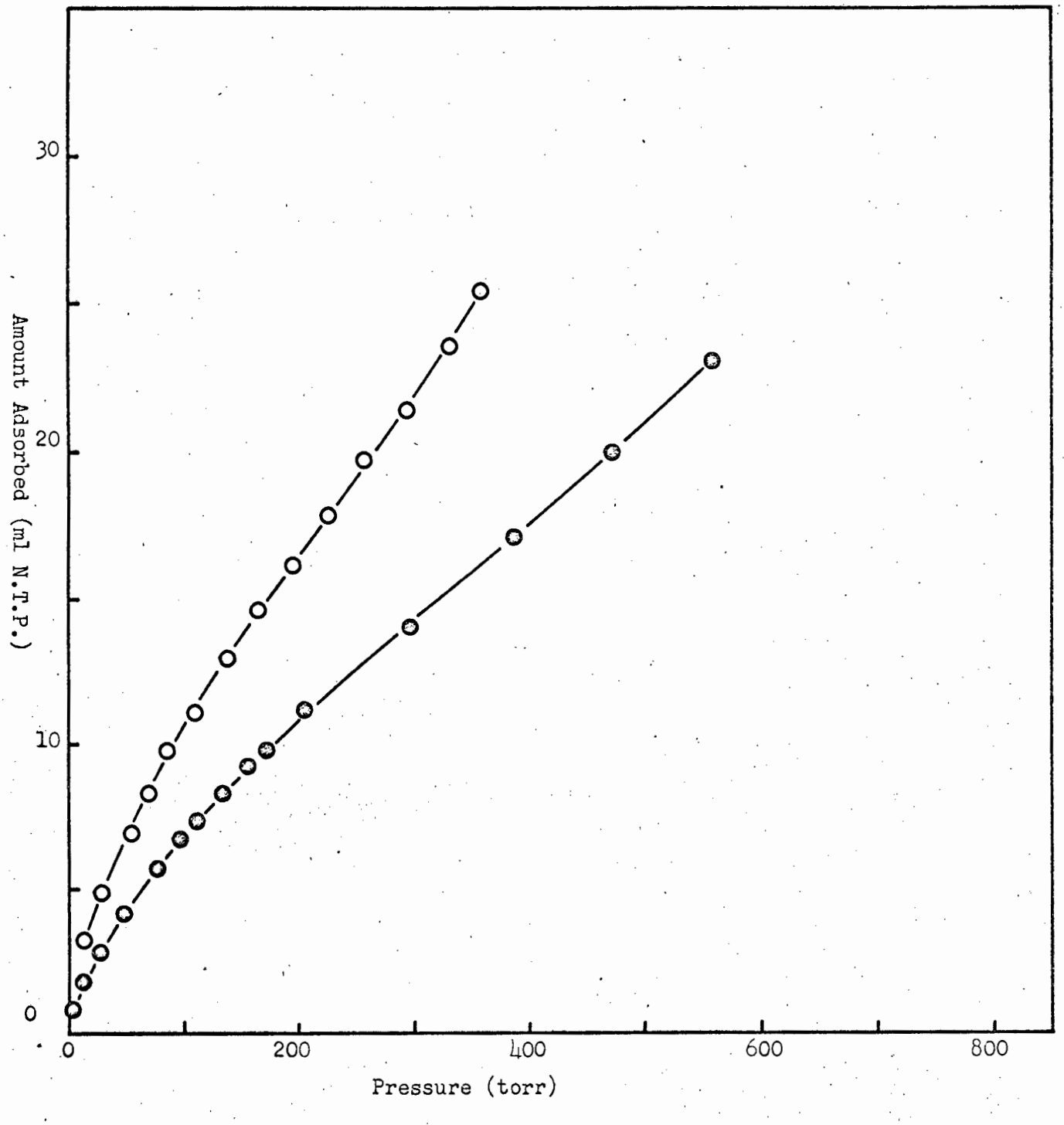


FIG. 38

ADSORPTION ISOTHERMS AT 25°C AND 42.0°C.

O = Run 76 at 25°C.

O = Run 69 at 42.0°C.



A third isotherm at 42.4°C was obtained in the manner described above, but after the highest pressure had been attained, the desorption branch was measured by reducing the pressure stepwise by removal of known amounts of monomer, and calculating the amount of monomer remaining on the surface 48 hours after the reduction in pressure. The results for this experiment are shown in Figure 39.

3.9 The surface area of the polymer sample.*

The surface area of the polymer was determined by the B.E.T. method using krypton at liquid nitrogen temperature. The volume of krypton required to form a monolayer on the surface was found to be 10.0 ml at N.T.P. The B.E.T. plot of $(p/p^{\circ})/[s(1 - \frac{p}{p^{\circ}})]$ against $\frac{p}{p^{\circ}}$ is shown in Figure 40. In the above expression p is the equilibrium pressure for an amount of krypton "s" adsorbed and p° is the saturated vapour pressure of krypton at liquid nitrogen temperature.

* Acknowledgements.

FIG. 39.

ADSORPTION - DESORPTION ISOTHERM AT 42.4°C.

⊙ = Adsorption Branch (Run 67)

O = Desorption Branch (Run 68)

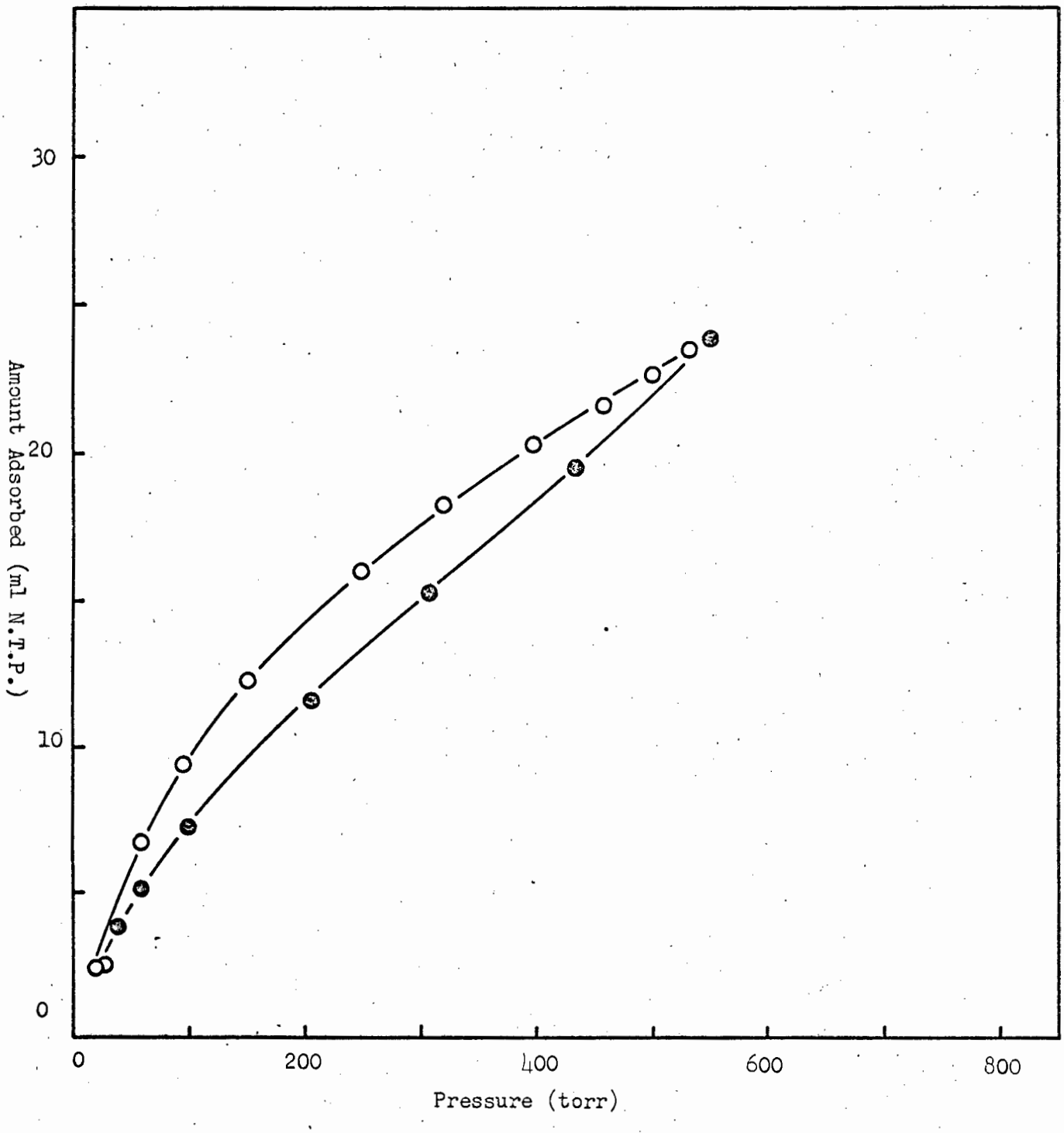
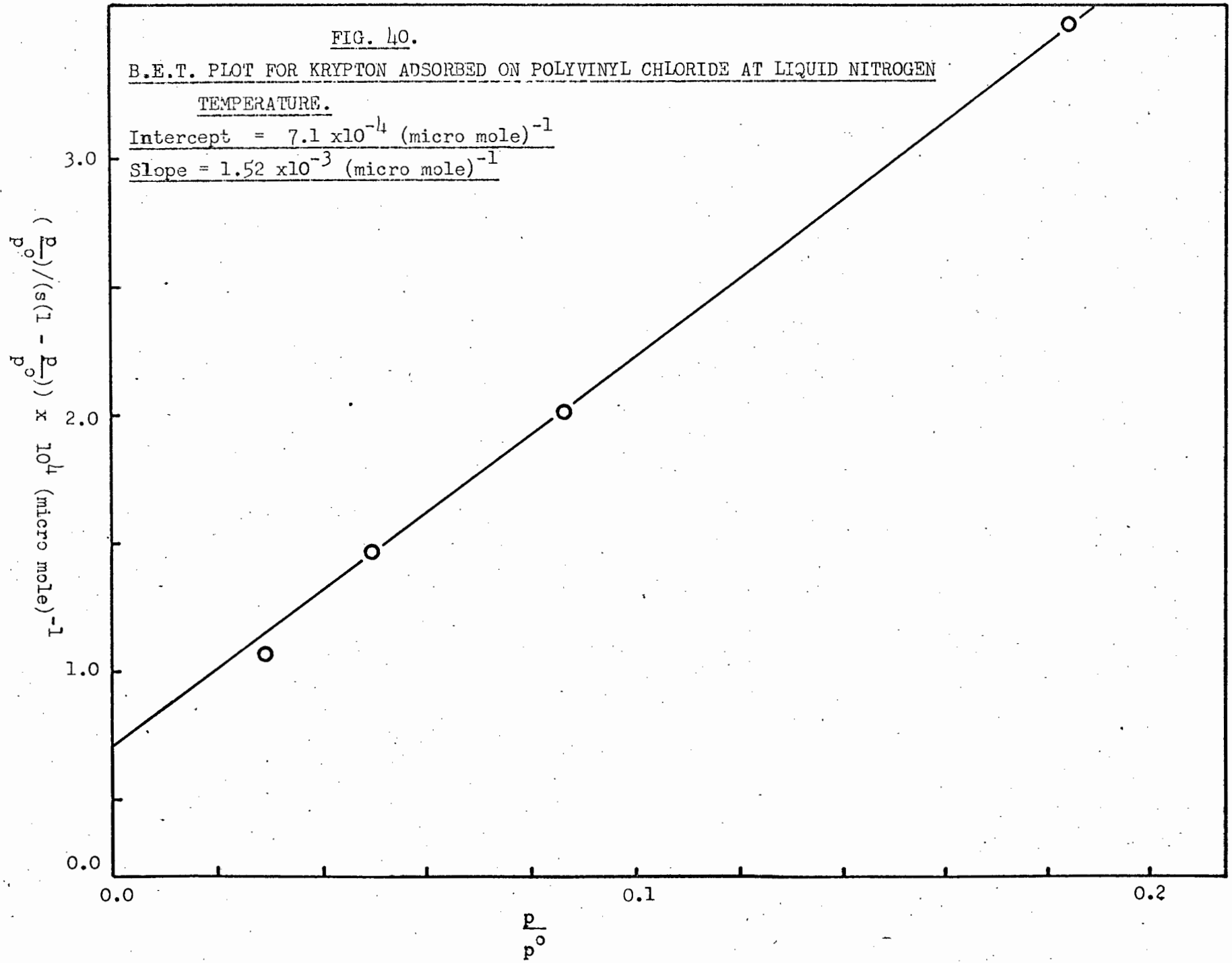


FIG. 40.

B.E.T. PLOT FOR KRYPTON ADSORBED ON POLYVINYL CHLORIDE AT LIQUID NITROGEN TEMPERATURE.

Intercept = 7.1×10^{-4} (micro mole)$^{-1}$

Slope = 1.52×10^{-3} (micro mole)$^{-1}$



CHAPTER 4.

Analysis of Kinetic Results for Vinyl Chloride on Polyvinyl Chloride.

4.1 Precision of the results.

The formula used when calculating the amount of monomer adsorbed at any time, using the apparatus in Figure 31, was as follows:

$$s_t = 0.35944\ p\left[\frac{D}{T_R} + \frac{V_g}{T_g} + \frac{M(41.00-A)}{T_R}\right] - 0.35944\ p'\left[\frac{D}{T_R} + \frac{V_g'}{T_g} + \frac{M(82-(A'+B))}{T_R}\right] - Fp'$$

In this expression the unprimed symbols pertain to conditions existing before the monomer is allowed to come into contact with the polymer. The primed symbols pertain to conditions existing at the time of measurement.

The pressure in the system could be read with an estimated error of 1 torr, the temperature of the room and the gas burette with an error of 0.1 K, A, A' and B with an error of 0.5 mm and V_g and V_g' with an error of 0.1 ml. The value of D had been determined as 37.71 ml ± 0.14 ml; the value of F was 1.604×10^{-2} ml N.T.P. $torr^{-1}$ ± 6×10^{-5} ml N.T.P. at 42.6°C and the value of M was 0.271 ml cm^{-1} ± 0.001 ml.

When these estimates of the errors in the measurements, together with the actual measurements, were substituted in the relationship for the propagation of errors [83] a calculated relative error of 1.2% was obtained for an amount of 21.4 ml N.T.P. of monomer adsorbed after 30 minutes at a pressure of 574 torr and a temperature of 42.6°C.

The actual observed reproducibility of the results was rather poor as can be seen from the figures shown in Table 4, where the amounts adsorbed after 30 minutes, for four runs done under similar conditions, are compared. This poor reproducibility was probably due to the surface not being degassed to the same extent for each run.

4.2 The rate curve.

The rate of adsorption at any time could be obtained by measuring the slope of the amount adsorbed against time curve at the point

TABLE 4.

Comparison of amounts adsorbed after 30 minutes for runs performed under similar conditions at 42.6°C.

Pressure of Run	Amount adsorbed
(Torr)	(ml N.T.P.)
578	20.83
578	21.28
574	21.45
579	21.91

Mean Value 21.37 ml N.T.P.

Standard deviation 0.45 ml N.T.P.

of interest. Determination of rates by this method is not always very precise because the methods employed for determining the slope of the curve usually demand a smooth curve with no breaks. As experimentally determined points always show some scatter, the actual smooth curve fitted to them is likely to be highly subjective. However examination of a rate curve can often lead to the formulation of some rate equation, the parameters of which can then be more precisely obtained by numerical operations on the actual experimental data.

With this in mind, one typical run at constant pressure and 42.6°C was chosen and the rates of adsorption at various amounts adsorbed measured. (Fig. 41). Two methods were used to obtain the slope of the "Amount adsorbed" against "Time" curve, viz., the mirror method[84] and the numerical five-point method.[84]

The apparent linearity of the "Amount adsorbed" against "log time" curves in the region beyond ten minutes suggested that a plot of "log rate" against "Amount adsorbed" should be linear over this range. This plot was made (Fig. 42) and it appeared to become linear as the amount adsorbed increased. However, in the beginning the plot was definitely curved, this curvature suggesting that some other process was occurring either simultaneously with the process which occurred in the later region or alone.

To test whether the two processes occurred simultaneously in the first ten minutes of the adsorption, the linear region of the "Amount adsorbed" against "log time" was extrapolated backwards towards lower values of time. The actual amount adsorbed at a given time was then subtracted from the extrapolated value at the same time. If two processes were occurring simultaneously then this difference would represent the amount still to be adsorbed by the second process before it attained

FIG. 41

PLOT OF RATE OF ADSORPTION AT 458 TORR AND 42.6°C AGAINST AMOUNT ADSORBED.

O = Mirror method
⊙ = 5 Point method

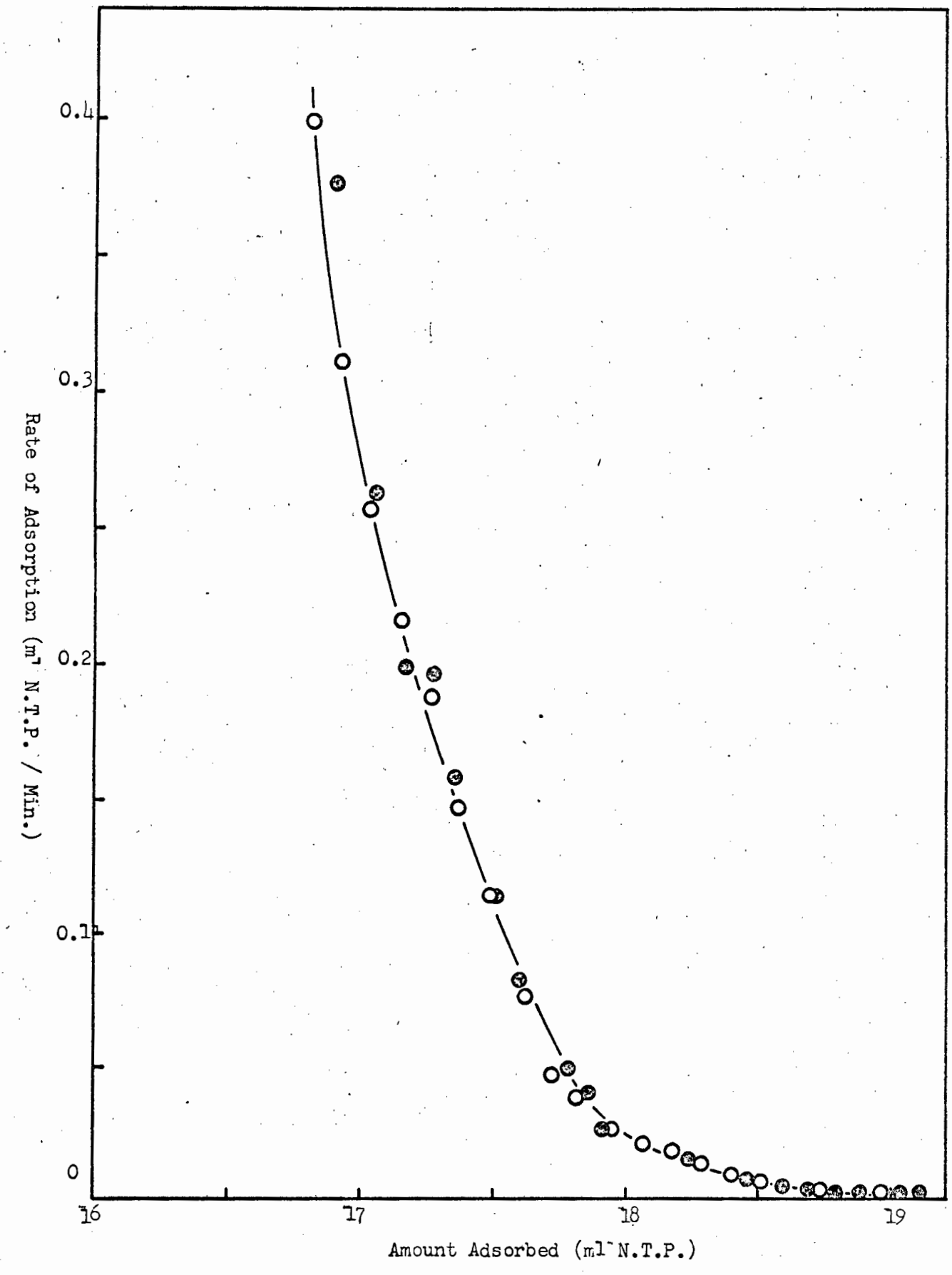
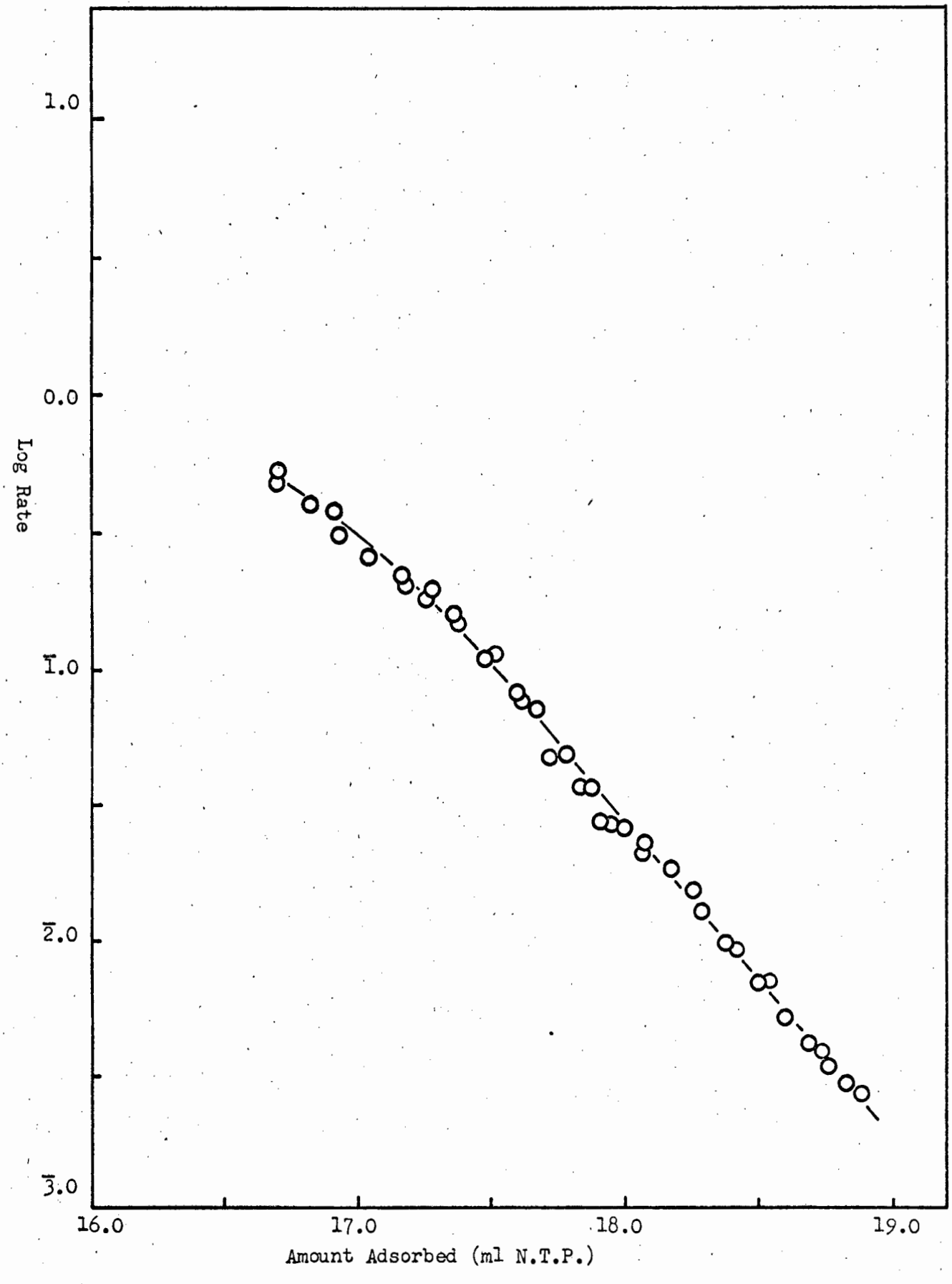


FIG. 42

PLOT OF LOG RATE AGAINST AMOUNT ADSORBED AT 458 TORR AND 42.6°C.



equilibrium. Various plots of this difference were made but all of them were curved and no simple relationship could be found.

The earlier region of the rate plot (Fig. 41) appeared to be parabolic and therefore a plot of "$(\text{Rate})^{\frac{1}{2}}$" against "Amount adsorbed" was tried (Fig. 43). This plot was definitely linear at earlier times and then after ten minutes or so became definitely curved, the point at which the plot became curved being very clearly marked amounting almost to a break in the curve. When the linear region of this curve was extrapolated to the $(\text{Rate})^{\frac{1}{2}} = 0$ axis, it cut this axis at an amount adsorbed equal to 18.33 ml. A plot of $(18.33 - \text{amount adsorbed})^{-1}$ against time (Fig. 44) was made and found to be linear over the first ten minutes or so of the reaction.

4.2.1 Conclusions drawn from the study of the rate curve.

The form of the rate curve seemed to indicate that:

(i) There were two measurable processes occurring.

(ii) In the first ten minutes or so there was a process occurring which obeyed the rate law $\frac{ds}{dt} = k_p(s_\infty - s)^2$ where k_p is a constant which may be pressure dependent and s_∞ is the equilibrium amount adsorbed by this process.

It also seemed that this process occurred alone in the first ten minutes and that the second process, which might be of the Elovich type, only commenced later, but before the first process had gone to completion, i.e., before s_∞ was attained, evidence for the late start of the possibly Elovich type process being the good fit of the experimental point to the rate equation quoted above and the sharp break exhibited by the $(\text{Rate})^{\frac{1}{2}}$ against amount adsorbed curve.

FIG. 43

PLOT OF $(RATE)^{\frac{1}{2}}$ AGAINST AMOUNT ADSORBED AT 458 TORR and 42.6°C.

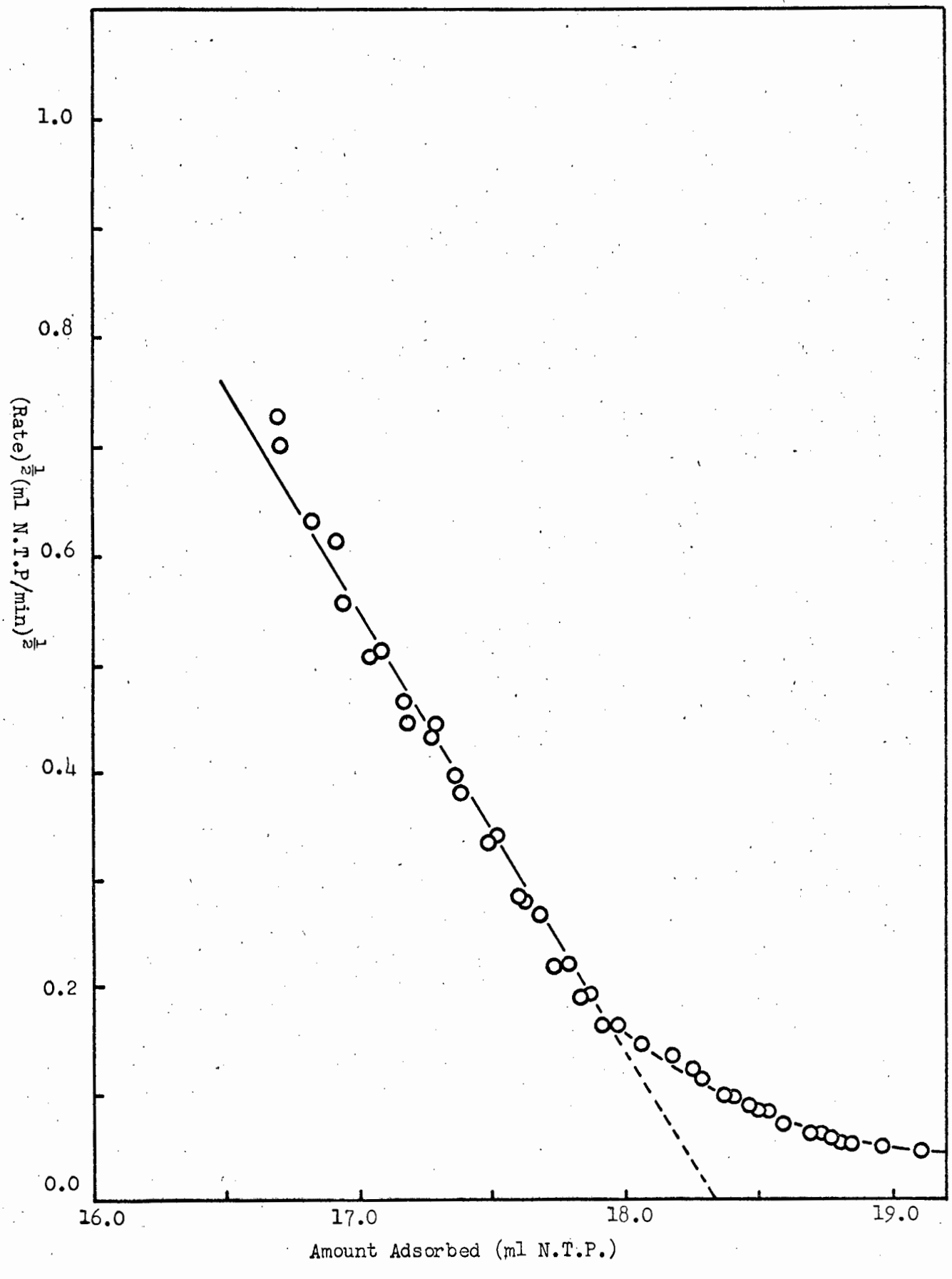
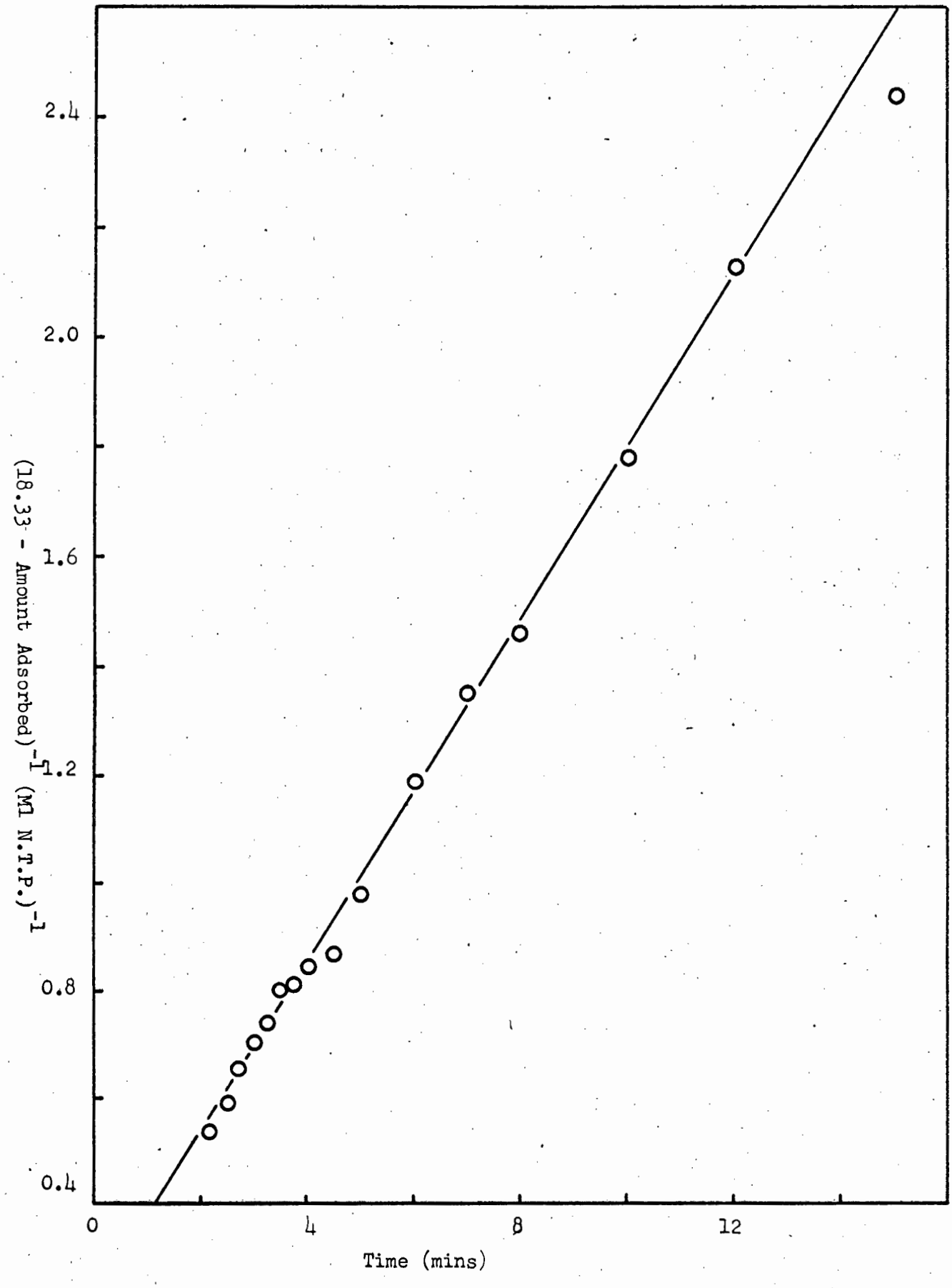


FIG. 44

PLOT OF $(18.33 - \text{AMOUNT ADSORBED})^{-1}$ AGAINST TIME AT 458 TORR AND 42.6°C



4.3 A numerical method for obtaining k_p and s_∞ from experimental points.

If the rate of adsorption obeys the relationship:

$$\frac{ds}{dt} = k_p(s_\infty - s)^2 \qquad \text{- - - - - - - - -} \qquad 1.$$

then on integration this gives:

$$\frac{1}{s_\infty - s} = k_p t + \text{const} \qquad \text{- - - - - - - - -} \qquad 2.$$

If two times, t_1 and t_2 are chosen then:

$$\frac{s_2 - s_1}{(s_\infty - s_2)(s_\infty - s_1)} = \frac{\Delta s}{(s_\infty - s_2)(s_\infty - s_1)} = k_p \Delta t$$

$$\therefore \quad \frac{\Delta s}{\Delta t} = k_p(s_\infty - s_2)(s_\infty - s_1)$$

If for a particular run t_2 is fixed at some value, for example at 10 minutes, then a plot of $\frac{\Delta s_t}{\Delta t_t}$ against s_t will be linear with slope $= -k_p(s_\infty - s_2)$ and the plot will cut the $\frac{\Delta s_t}{\Delta t_t} = 0$ axis at $s_t = s_\infty$.

$(\Delta s_t = s_2 - s_t,\ \Delta t_t = t_2 - t)$

4.3.1 Application of the numerical method to runs at constant pressure and 42.6°C.

The method given in section 4.3 was applied to the runs done at constant pressure and 42.6°C. The procedure adopted was as follows:

A plot was made of "Amount adsorbed" against "Time" and a smooth curve fitted by inspection to the experimental points. This plot was made so that points which were obviously out could be corrected, otherwise the actual experimental points were used in the application of the numerical method. s_2 and t_2 were now chosen, these usually being the amount adsorbed at ten minutes. $\frac{\Delta s_t}{\Delta t_t}$ was then calculated for each of the experimental points and plotted against s_t (Fig. 45 and Fig. 46). From the slopes and intercepts of these plots k_p and s_∞ could be calculated for each run. Some of the values obtained for k_p and s_∞ were checked by plotting $(\text{Rate})^{\frac{1}{2}}$ against amount adsorbed and the agreement between the two methods was

FIG. 45

PLOT OF $\frac{\Delta s}{\Delta t}$ AGAINST s_t FOR RUN 58 AT 580 TORR and 42.6°C

Slope of Plot = - 0.075 $mins^{-1}$

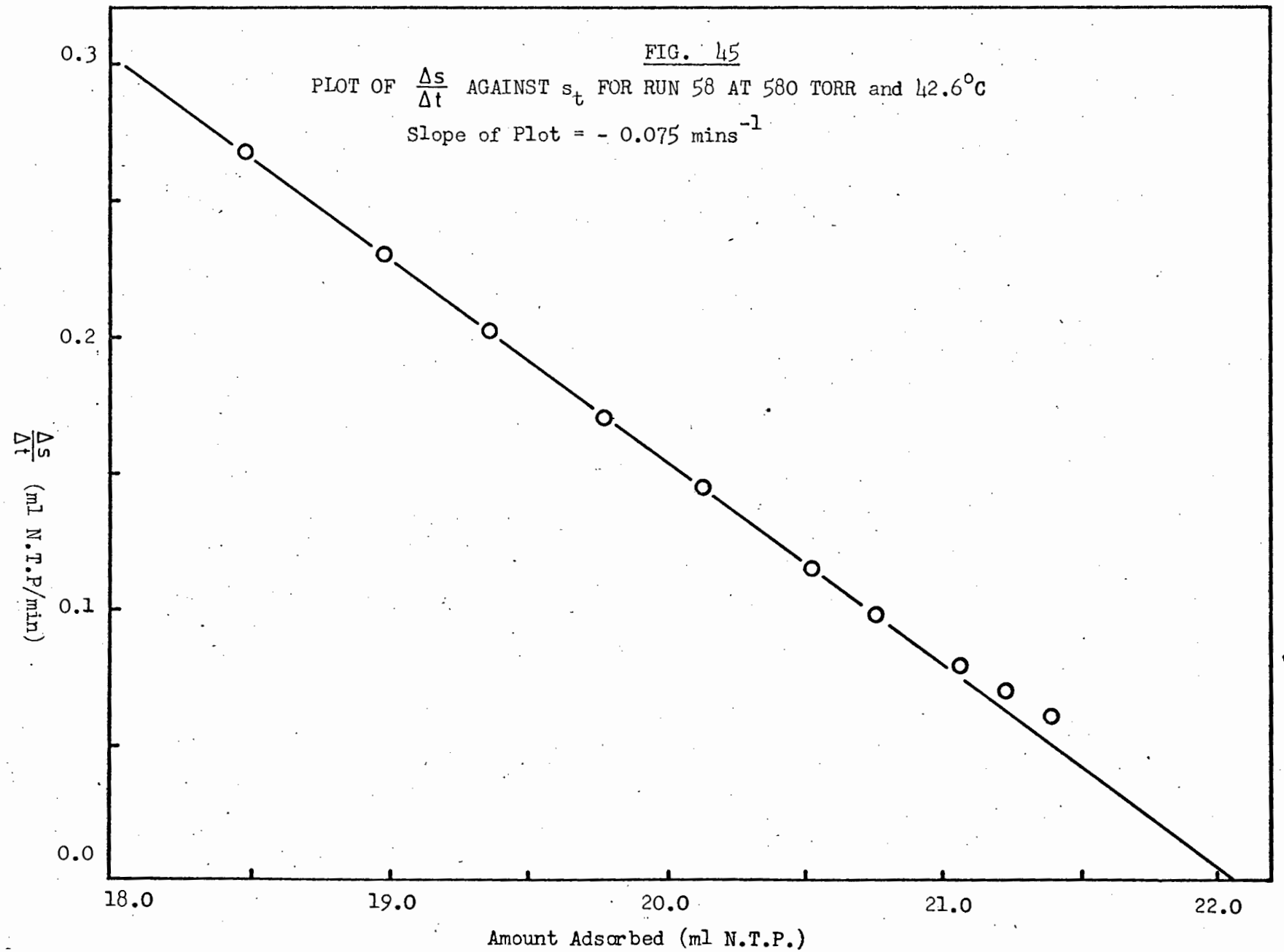
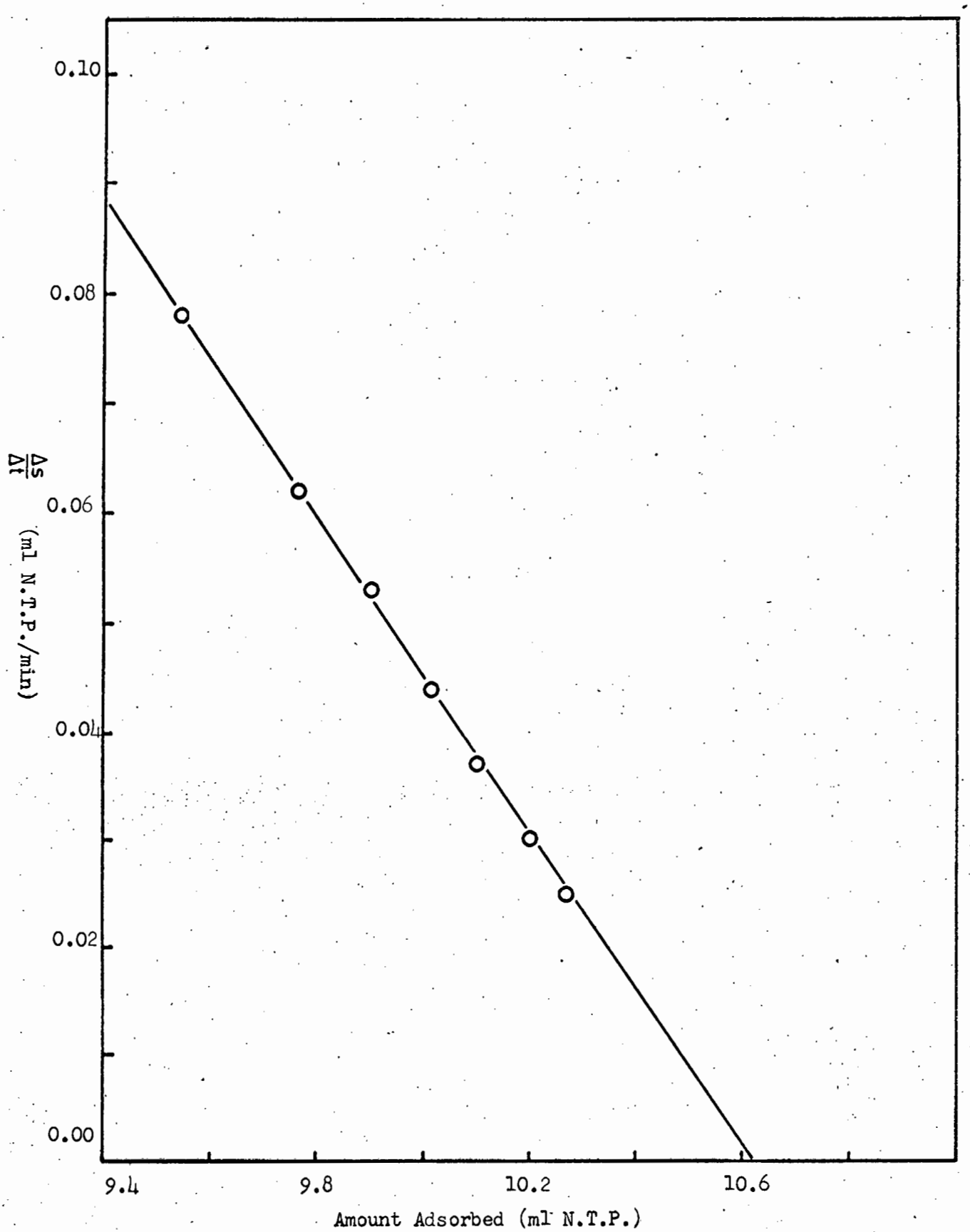


FIG. 46

PLOT OF $\frac{\Delta s}{\Delta t}$ AGAINST s_t FOR RUN 44 AT 213 TORR and 42.6°C

Slope of Plot = - 0.073 $mins^{-1}$



found to be good. Table 5 shows the results obtained. Plots of $(s_\infty - s_t)^{-1}$ against "time" were also made (Fig. 47) and shown to be linear, the value of k_p calculated from these plots being in good agreement with the values of k_p obtained from the numerical method. Table 5 and Figure 47 show that:

(i) k_p decreases with increasing pressure;

(ii) s_∞ increases with increasing pressure.

One significant point arose from a study of the $\frac{\Delta s_t}{\Delta t_t}$ plots, namely, that for those plots in which t_2 had the same value, the slopes of the plots were identical, i.e., $k_p(s_\infty - s_2)$ was the same for all runs. This means that $k_p(s_\infty - s_2)$ was independent of pressure. As k_p, s_∞ and s_2 are all pressure dependent their pressure dependence must be of the form:

$$s_\infty = af(p), \quad s_2 = bf(p), \quad k_p = \frac{k}{f(p)}$$

where a is a constant, k is a constant and $b = b(t_2)$. As s_2 is an arbitrarily chosen value it follows that $s_t = b(t\ )f(p)$.

4.4 Pressure dependence of s_∞, s_t and k_p.

A plot of log k_p against log pressure (Fig. 48) was found to be linear and gave a least square slope of -0.68. Hence $k_p = \frac{C}{p^{.68}}$. Plots of amount adsorbed at constant time against pressure were made (Fig. 49) and within experimental scatter the points lay on smooth curves. It was interesting to note that points obtained from runs 70, 73 and 75, done under constant volume conditions, also lay on the same curves. Replotting the data of Figure 49 as log s_t against log pressure (Fig. 50) parallel straight lines of slope 0.72 were obtained, this value of 0.72 being in good numerical agreement with the value of -0.68 obtained for the plot of log k_p against log pressure.

Log s_t against log pressure plots were also made for runs done at 25°C under constant volume conditions (Fig. 51). These plots were also

FIG. 47

PLOT OF $(s_\infty - s)^{-1}$ AGAINST TIME FOR RUNS AT DIFFERENT PRESSURES AND 42.6°C

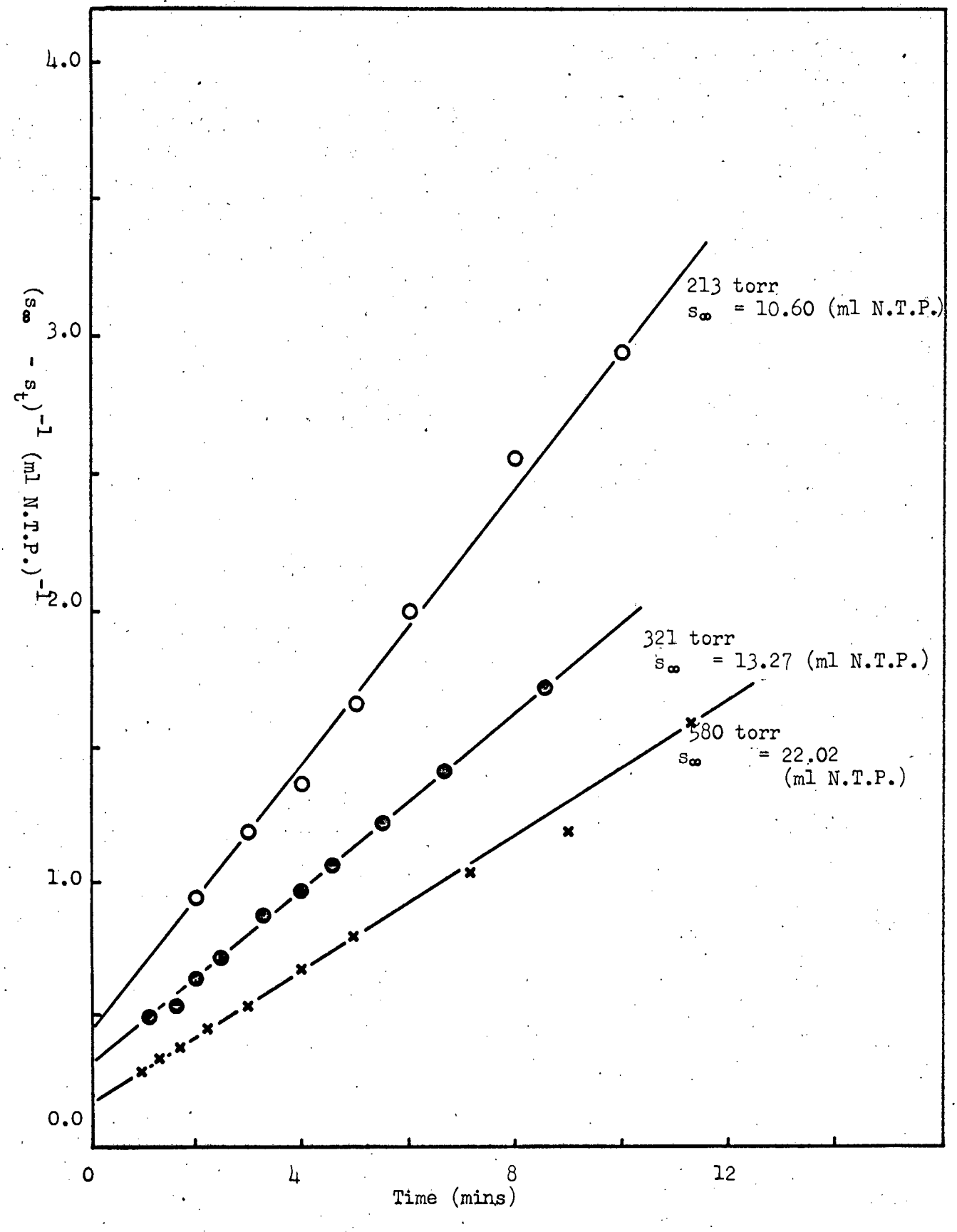


TABLE 5

Calculated values of s_∞ and k_p for runs at constant pressure at 42.6°C.

Run No.	Pressure	s_∞	k_p
	(torr)	(ml N.T.P.)	$(\text{ml N.T.P.})^{-1}(\text{min})^{-1}$
40	559	21.28	0.120
41	458	18.79	0.138
42	387	16.48	0.149
43	297	13.32	0.190
44	213	10.63	0.232
46	560	20.07	0.121
47	458	18.39	0.136
48	404	16.65	0.158
49	312	13.88	0.177
50	222	10.60	0.252
51	321	13.24	0.176
53	121	6.92	0.334
54	578	20.88	0.117
55	578	21.45	0.122
58	579	22.03	0.119
60	570	22.08	0.121

FIG. 50

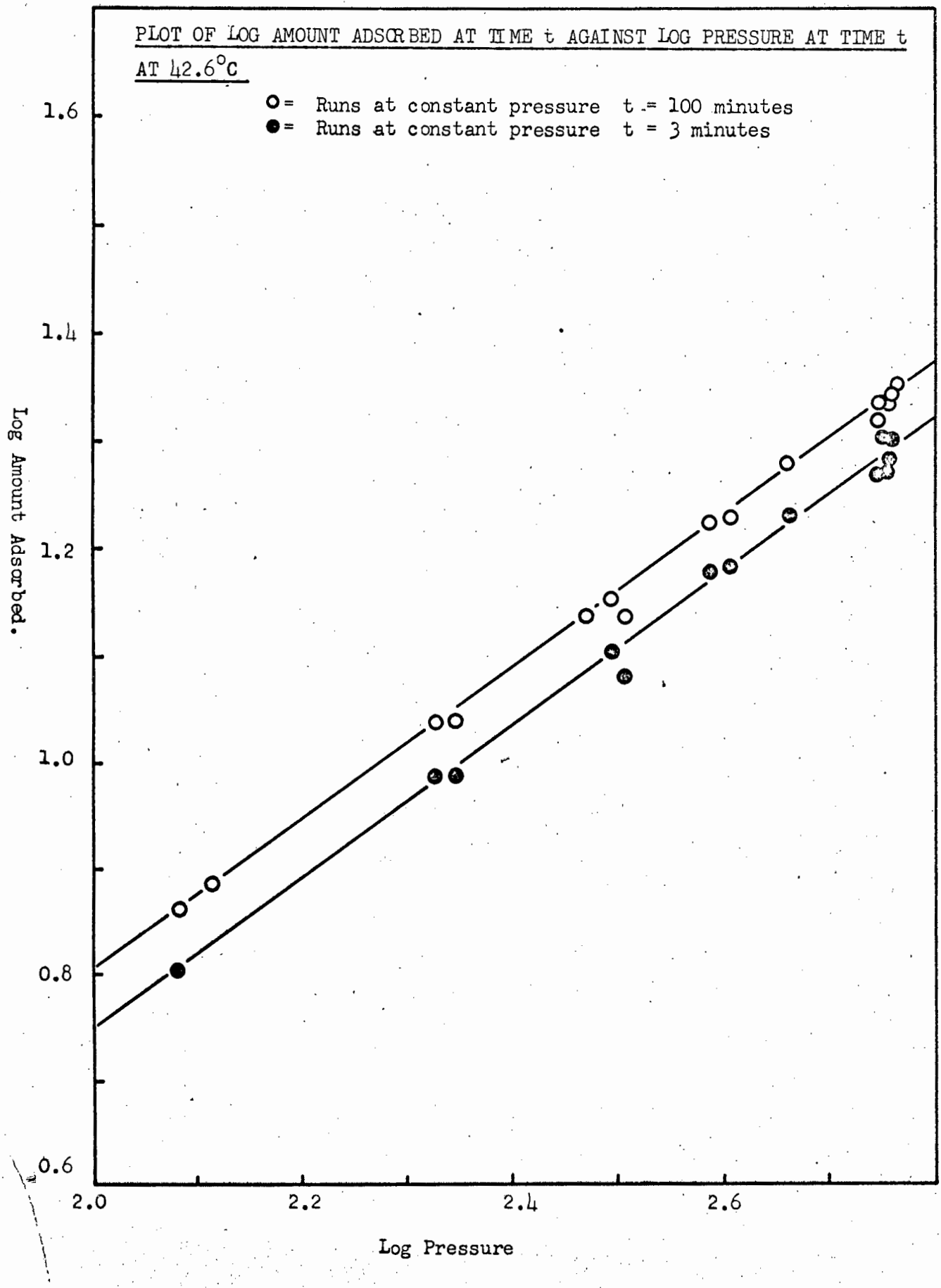
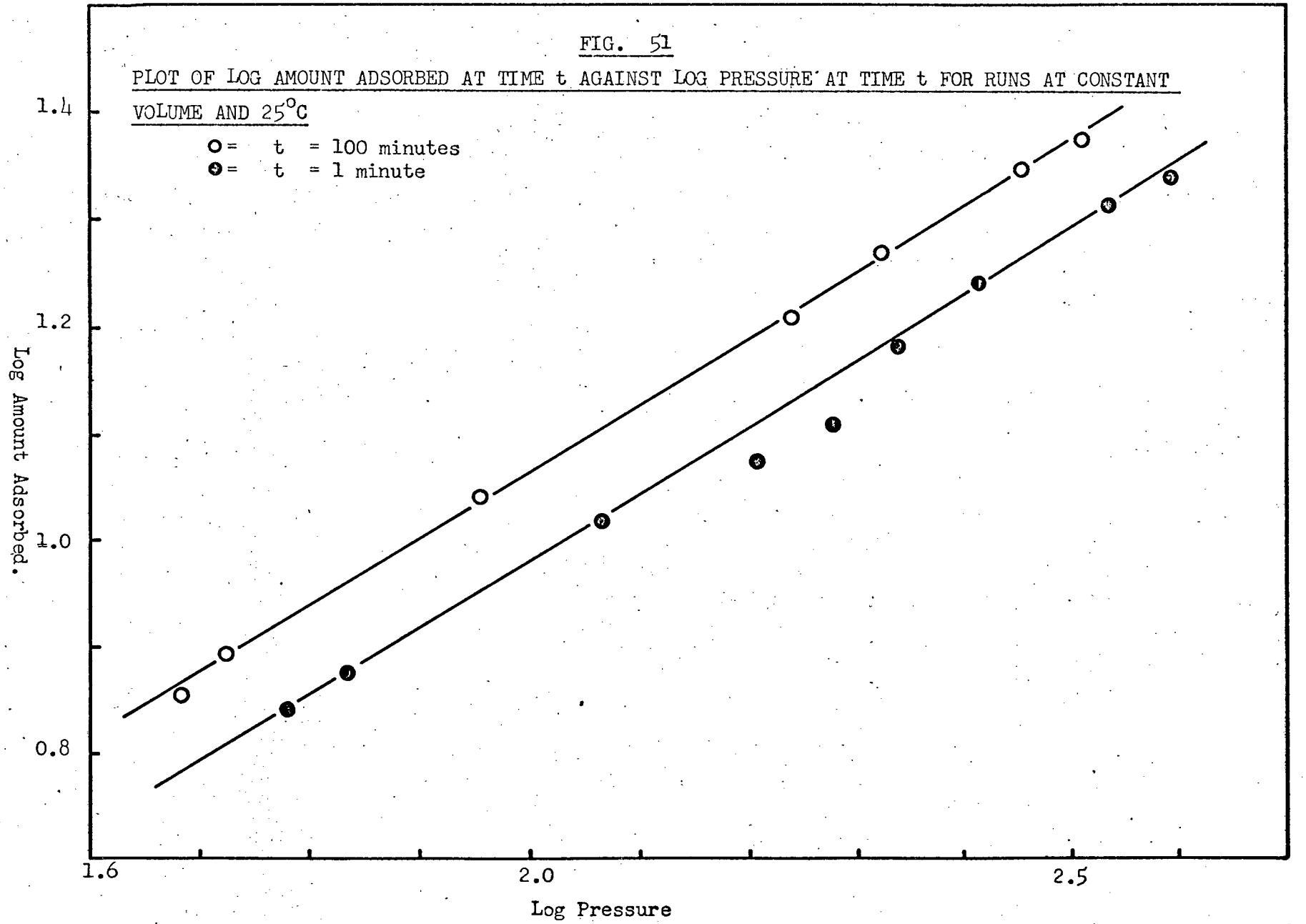

PLOT OF LOG AMOUNT ADSORBED AT TIME t AGAINST LOG PRESSURE AT TIME t AT 42.6°C
O = Runs at constant pressure t = 100 minutes
● = Runs at constant pressure t = 3 minutes
1.6
1.4
1.2
1.0
0.8
0.6
Log Amount Adsorbed.
2.0
2.2
2.4
2.6
Log Pressure

FIG. 51

PLOT OF LOG AMOUNT ADSORBED AT TIME t AGAINST LOG PRESSURE AT TIME t FOR RUNS AT CONSTANT VOLUME AND 25°C



found to be linear and parallel with slope 0.62. The least square slopes for log s_t against log pressure plots for several times at both 42.6°C and 25°C are recorded as m in Table 6. This table shows that m is constant at constant temperature having a mean value of 0.62 at 25°C and 0.72 at 42.6°C.

Further evidence for the correctness of the proposed variation of s_t with pressure can be obtained by replotting the data of Figure 34 (section 3.7) and Figure 36 (section 3.8) as $\frac{s}{p^{.62}}$ against log t (Figs. 52 and 53). These plots were now continuous and apparently linear with no sign of the break shown in Figures 34 and 35 at the point where the conditions were altered.

It should be possible to calculate the value of m from the data for Figure 34, the reasoning being as follows:

As s_t plotted against pressure gives a smooth curve

$s = f(p,t)$

If this function is of the form $s = p^m b(t)$

then $b(t) = \frac{s}{p^m}$

The rate of adsorption at constant volume $(\frac{ds}{dt})_v$ will be given by

$$(\frac{ds}{dt})_v = p^m \frac{\partial b(t)}{\partial t} + m\, b(t) p^{m-1} \frac{dp}{dt} \quad \text{- - - - - - - - -} \quad \text{A.}$$

The rate of adsorption at constant pressure $(\frac{ds}{dt})_p$ will be given by

$$(\frac{ds}{dt})_p = p^m \frac{\partial b(t)}{\partial t} \quad \text{- - - - - - - - - - - - - - - -} \quad \text{B.}$$

At constant volume $s = c - np$ where c and n are constants of the apparatus and the initial conditions.

$$\therefore (\frac{ds}{dt})_v = -n\frac{dp}{dt}.$$

$$\therefore \frac{dp}{dt} = -\frac{1}{n}(\frac{ds}{dt})_v \quad \text{- - - - - - - - - - - - - - - -} \quad \text{C.}$$

TABLE 6.

Values of m.

Time (mins.)	Temperature	
	25°C	42.6°C
1	0.615	0.729
10	0.631	0.736
20	0.629	-
50	0.622	0.722
100	0.619	0.719
200	0.616	0.716
500	0.615	-
1000	0.614	-
4300	0.617	-

FIG. 52

PLOT OF $s/p^{0.62}$ AGAINST LOG TIME FOR RUN 77 AT 25°C

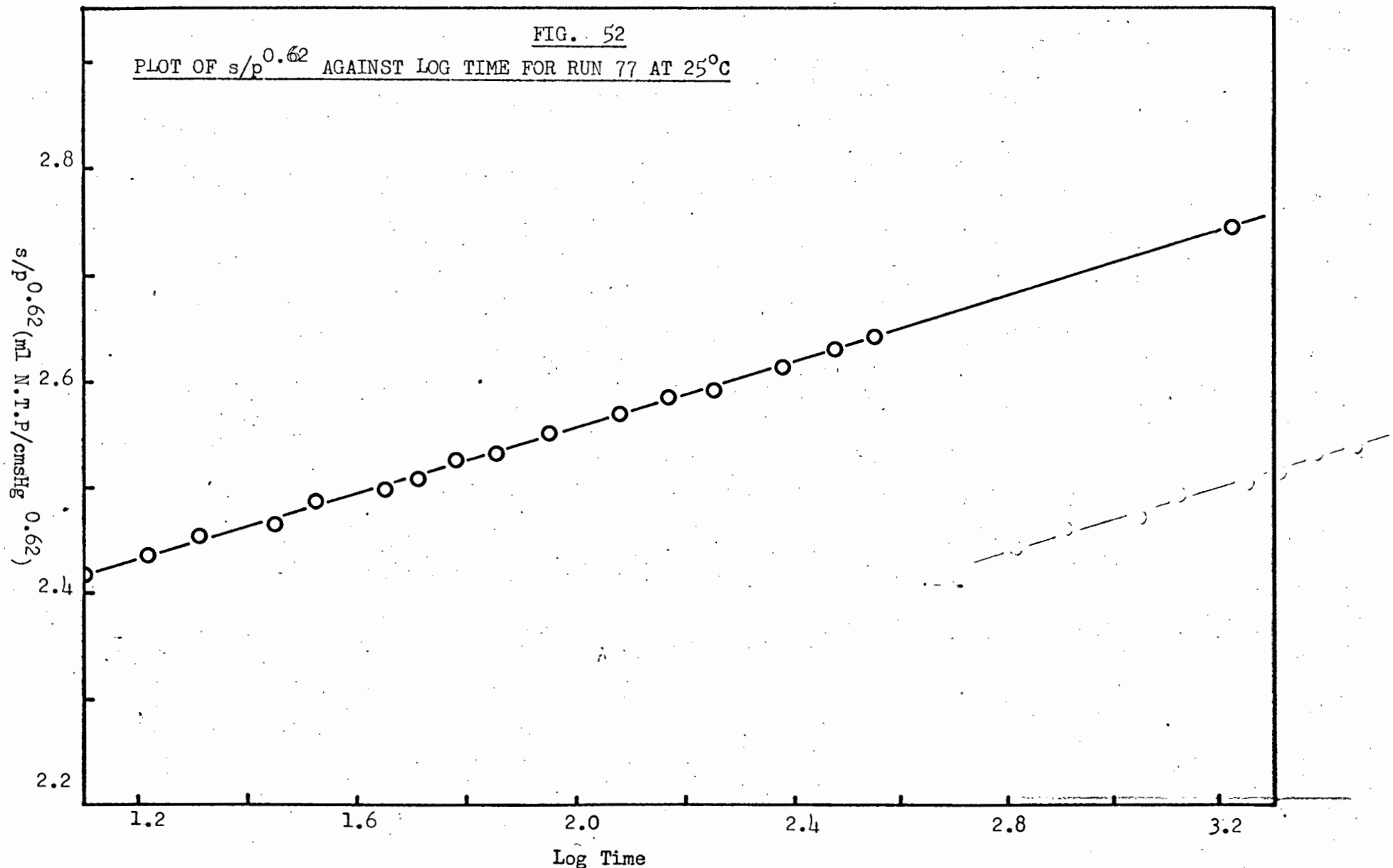
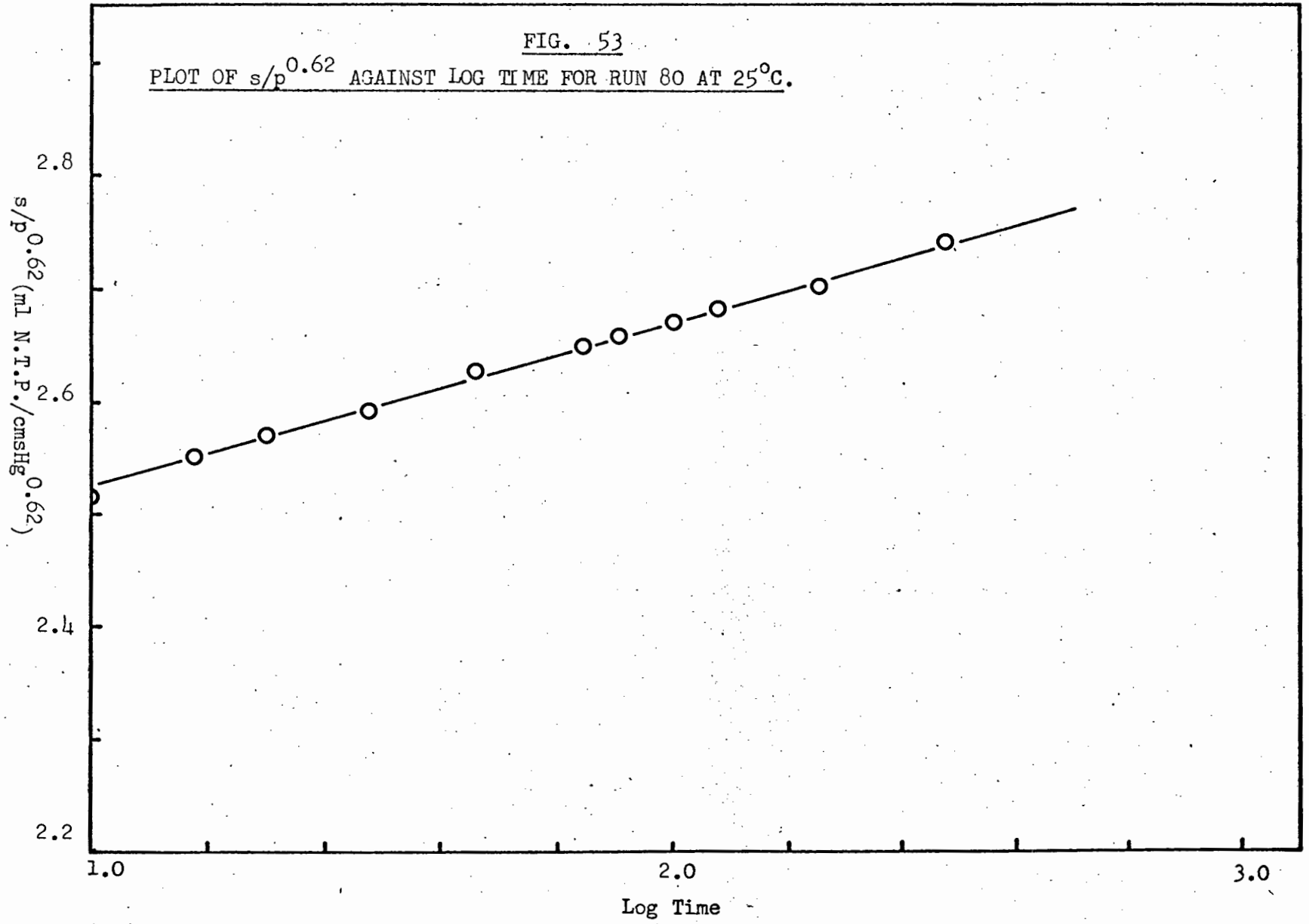


FIG. 53

PLOT OF $s/p^{0.62}$ AGAINST LOG TIME FOR RUN 80 AT 25°C.



Substitution of equation C in equation A gives

$$\left(\frac{ds}{dt}\right)_v \left[1 + \frac{m}{n} b(t)p^{m-1}\right] = p^m \frac{\partial b(t)}{\partial t} = \left(\frac{ds}{dt}\right)_p$$

$$\therefore \left(\frac{ds}{dt}\right)_p \Big/ \left(\frac{ds}{dt}\right)_v = 1 + \frac{m}{n} b(t)p^{m-1} = Z \quad \text{- - - - - - - - - - D.}$$

Substituting $b(t) = \frac{s}{p^m}$ in equation D gives

$$Z = 1 + \frac{ms}{np}$$

Hence

$$m = \frac{(Z-1)p \times n}{s} \quad \text{- - - - - - - - - - - - - - - - - - E.}$$

At the break in the curve where the conditions were changed from those at constant pressure to those at constant volume, the curve had two slopes. The ratio of these two slopes = Z.

Hence Z can be found for a given s_t and p_t, n can be obtained from the dimensions of the apparatus. Substitution of these values in equation E should enable m to be determined.

This was tried on run 77. For this run at 25°C Z = 2.19, n = 0.32, s_t = 29.57 and p_t = 52.6. Substitution of these values in equation E gives m = 0.68 in reasonable agreement with the value of 0.62 obtained earlier from the log s_t against log p_t plots.

Table 7 summarises the variation of k_p and s_∞ with pressure for the runs done at constant pressure and 42.6°C. The constancy of the values listed in columns 3 and 4 of the table being a verification of the hypothesis.

4.5 Application of the numerical method to runs at constant volume.

It was shown in section 4.4 that the amounts adsorbed at constant time plotted against pressure at the same temperature all lie on the same curve irrespective of whether the runs were done under constant pressure or constant volume conditions. It was also shown that the relationship between

TABLE 7

Pressure dependence of s_∞ and k_p for runs at constant pressure at 42.6°C.

Run No.	(Pressure)$^{0.724}$ = $p^{0.724}$ ((cms Hg)$^{0.724}$)	$k_p \times p^{0.724}$ ((ml N.T.P.)$^{-1}$ (cms Hg)$^{0.724}$) min^{-1}	$\frac{s_\infty}{p^{0.724}}$ (ml N.T.P. (cms Hg)$^{-0.724}$)
40	18.4	2.21	1.16
41	15.9	2.19	1.18
42	14.1	2.10	1.17
43	11.7	2.22	1.14
44	9.2	2.13	1.16
46	18.4	2.23	1.09
47	15.9	2.16	1.16
48	14.6	2.28	1.14
49	12.1	2.14	1.15
50	9.4	2.37	1.13
51	12.3	2.16	1.08
53	6.1	2.04	1.13
54	18.9	2.21	1.10
55	18.9	2.31	1.13
58	18.9	2.25	1.17
60	18.7	2.26	1.18

Mean value $k_p \times p^{0.724}$ = 2.20 (ml N.T.P.)$^{-1}$(cms Hg)$^{0.724}$ min^{-1}

Standard deviation of mean = 0.02 (ml N.T.P.)$^{-1}$(cms Hg)$^{0.724}$ min^{-1}

Mean value $\frac{s_\infty}{p^{0.724}}$ = 1.14 (ml N.T.P)(cms Hg)$^{-0.724}$

Standard deviation of mean = 0.01 (ml N.T.P.)(cms Hg)$^{-0.724}$

s_t and p_t was of the form $s_t = p_t^m b(t)$, b(t) being independent of pressure.

The numerical method of section 4.3 was applied directly to the data for run 70 at constant volume and 42.6°C (Fig. 54). As can be seen from the figure, the plot obtained was not linear. However, when the numerical method was applied to $\frac{s}{p^{.72}}$ values calculated from the same data the plot was linear (Fig. 55), cutting the $\Delta\frac{s}{p^{.72}} \Big/ \Delta t = 0$ axis at $\frac{s}{p^{.72}} = 1.129$. Plotting $(1.129 - \frac{s}{p^{.72}})^{-1}$ against time for the same run gives a linear plot (Fig. 56), i.e., at constant volume $\frac{s}{p^{.72}}$ behaves as does s at constant pressure, thus the relationship

$$\frac{d(\frac{s}{p^{.72}})}{dt} = k(a - \frac{s}{p^{.72}})^2$$ should hold, under both sets of conditions at 42.6°C.

Table 8 shows values of k and a, calculated as indicated above for runs done at constant volume at temperatures of 25°C and 42.6°C. The values shown for k and a in Table 8 for runs 70, 73 and 75 (with the exception of k for run 70) are in good agreement with the values of $k_p \times p^{.72}$ and $\frac{s_\infty}{p^{.72}}$ respectively shown in Table 7.

It can be concluded that in the first ten minutes or so of the reaction the rate, at constant pressure, follows the relationship:

$$\frac{ds}{dt} = kp^m(a - \frac{s}{p^m})^2$$ where a and k are constants.

4.6 The post ten minute region of the adsorption.

Analysis of this region was more difficult and less satisfactory than the pre ten minute region, because by this time the rate had become very slow and precision illusory. Most of the constant pressure runs at 42.6°C plotted as "Amount adsorbed" against "log time" appeared to be linear in this region over the period of measurement of approximately 300 minutes.

FIG. 54

PLOT OF $\frac{\Delta s}{\Delta t}$ AGAINST AMOUNT ADSORBED FOR RUN 70 AT CONSTANT VOLUME AND 42.6°C

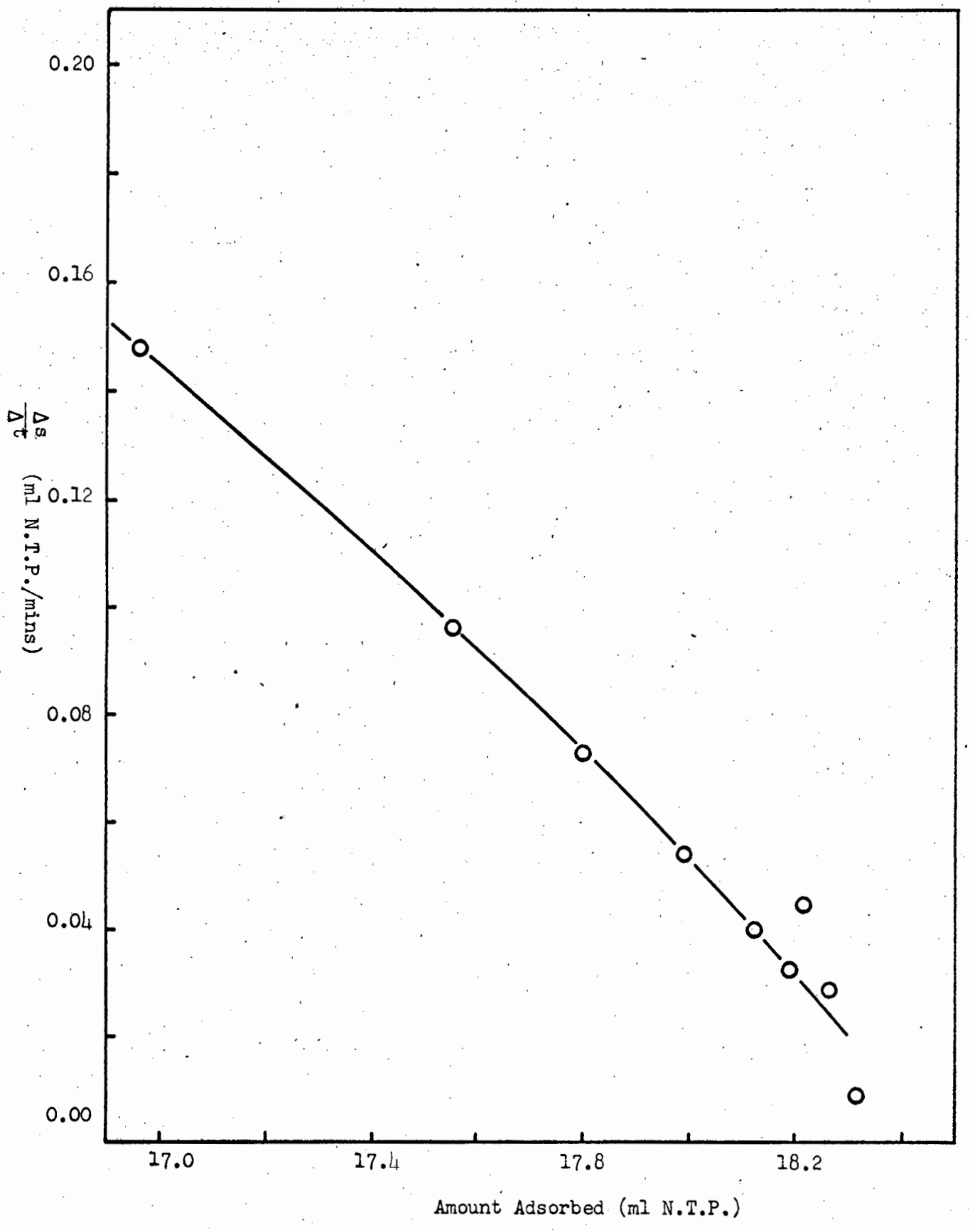


FIG. 55

PLOT OF $\frac{\Delta s/p^{.724}}{\Delta t}$ AGAINST $s/p^{.724}$ FOR RUN 70 AT CONSTANT VOLUME AND 42.6°C

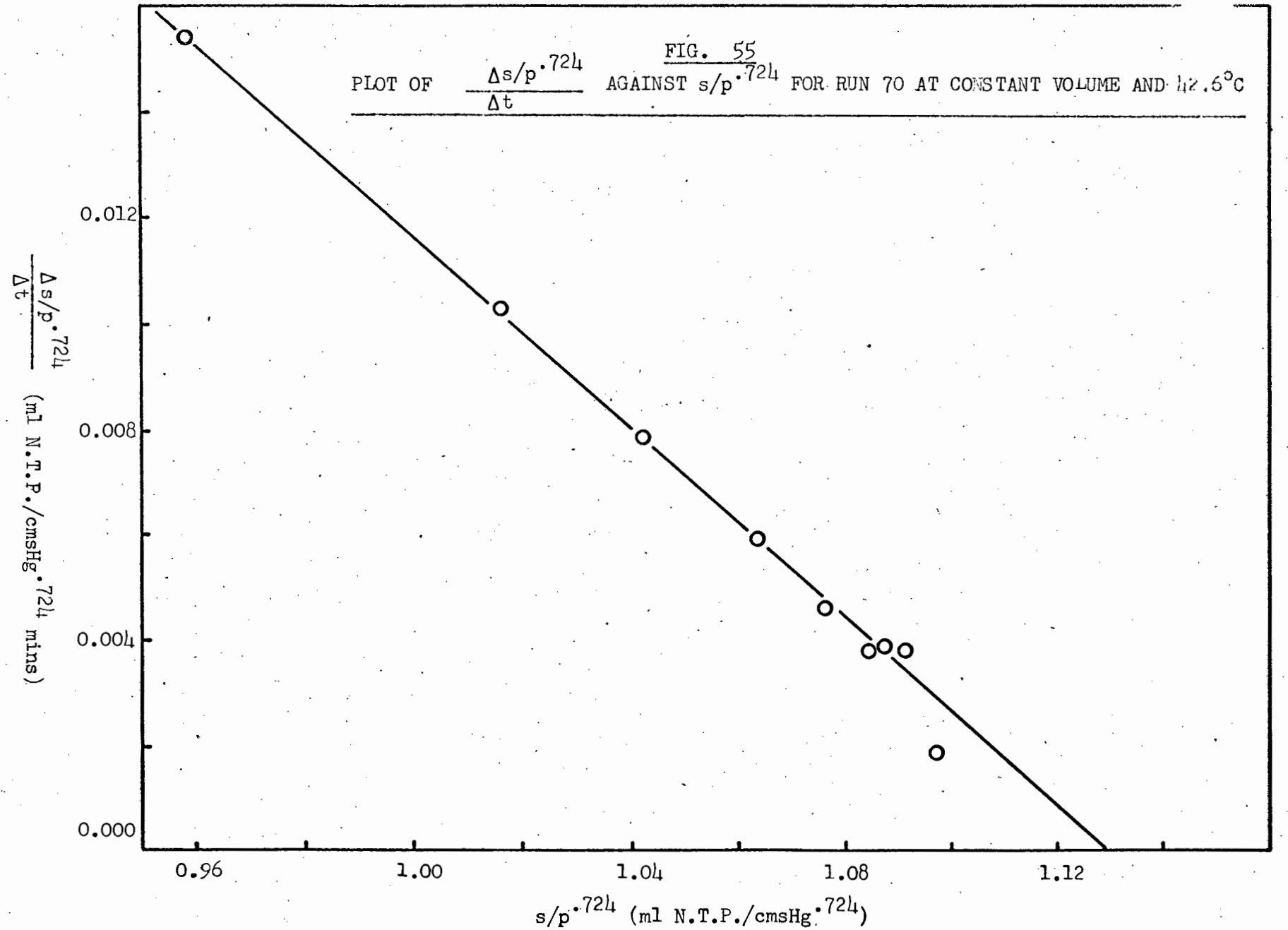


FIG. 56

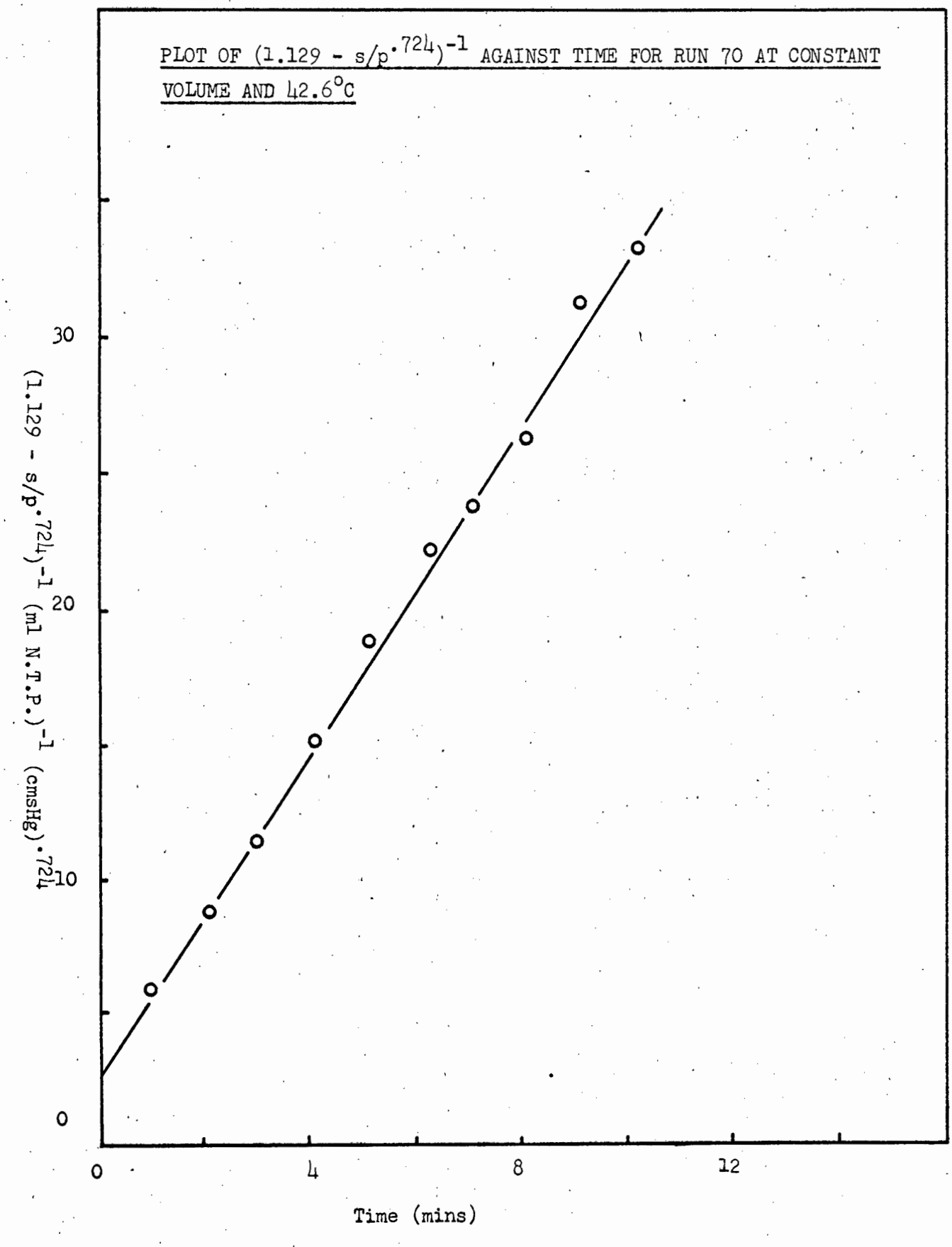

PLOT OF $(1.129 - s/p^{.724})^{-1}$ AGAINST TIME FOR RUN 70 AT CONSTANT VOLUME AND 42.6°C
$(1.129 - s/p^{.724})^{-1}$ (ml N.T.P.)$^{-1}$ (cmsHg)$^{.724}$
0
10
20
30
0
4
8
12
Time (mins)

TABLE 8.

Values of k and a calculated for runs at constant volume.

Run No.	Temperature ^{o}C	a	k $(ml)^{-1}(cm\ Hg)^{m}(min)^{-1}$	m
70	42.6	1.13	2.98	0.72
73	42.6	1.17	2.16	0.72
75	42.6	1.15	2.00	0.72
85	25.0	2.74	1.09	0.62
86	25.0	2.80	1.24	0.62
87	25.0	2.81	1.12	0.62
88	25.0	2.74	1.08	0.62
89	25.0	2.72	1.28	0.62
90	25.0	2.70	1.30	0.62
91	25.0	2.62	1.36	0.62

However, the constant volume curves, which were followed for a much longer time, even when plotted as $\frac{s}{p^m}$ against log time, showed definite curvature in this region tending to be concave towards the log time axis.

In the analysis which follows it was decided, because of the scatter in individual runs, to work with mean values of $\frac{s}{p^m}$. This is justified by the observation that the log amount adsorbed at constant time against log pressure appeared to be linear and parallel up to large values (4000 minutes) of time. Mean values of $\frac{s}{p^m}$ at various times are tabulated together with the standard deviation of the mean in Tables 9 and 10, and a plot of mean $\frac{s}{p^{.62}}$ against log time for the values obtained at 25°C is shown in Figure 57.

The first ten minutes of the mean curves were analysed using the numerical method of section 4.3. The Δmean $\frac{s}{p^m}/\Delta t$ plots being shown in Figures 58 and 59. These were linear and gave numerical values of k of 1.22 and 2.47 and numerical values of $\frac{s_\infty}{p^m}$ of 2.706 and 1.139 at 25°C and 42.6°C respectively, in fair agreement with the individually measured results.

It was now assumed that both processes occur simultaneously in the post ten minute period. Values of $\frac{s}{p^m}$ were calculated for the first process using the values quoted above. Subtraction of these from the actually measured values of $\frac{s}{p^m}$ gave $\frac{s}{p^m}$ values for the second process. This difference was then plotted against log time in the case of the results for 25°C (Fig. 60) and log (time + 3 minutes) in the case of the results at 42.6°C (Fig. 61). These plots were found to be linear with slopes of 0.112 and 0.055 at 25°C and 42.6°C respectively.

The plots (Figs. 60 and 61) cut the log time axis at 16 and 20 minutes respectively. Thus the second process appeared to start 16 and 17 minutes respectively after the start of the adsorption. Hence the

TABLE 9.

Mean Values of $\frac{s}{p^{.62}}$ for runs 85 to 90 at constant volume at 25°C.

Time	Mean $\frac{s}{p^{.62}}$	Std. deviation of Mean
(mins)	(ml N.T.P.) $(cmHg)^{-0.62}$	
1	2.287	0.013
2	2.419	0.014
3	2.493	0.016
4	2.541	0.015
5	2.569	0.017
7	2.608	0.015
10	2.631	0.016
15	2.663	0.015
20	2.675	0.015
30	2.707	0.014
50	2.739	0.012
100	2.782	0.010
200	2.824	0.011
1000	2.905	0.009
4300	2.971	0.004

TABLE 10.

Mean Values of $\frac{s}{p^{.724}}$ for runs 40 - 60 at constant pressure at 42.6°C.

Time	Mean $\frac{s}{p^{.724}}$	Std. deviation of mean
(mins.)	(ml N.T.P.) $(cmHg)^{0.724}$	
2	1.015	0.008
3	1.045	0.007
4	1.063	0.007
5	1.074	0.007
7	1.090	0.007
10	1.103	0.007
15	1.116	0.007
20	1.124	0.007
30	1.138	0.007
40	1.147	0.007
50	1.154	0.007
75	1.166	0.007
100	1.174	0.007
150	1.184	0.007
200	1.192	0.006
300	1.203	(4 results only)

FIG. 57

PLOT OF MEAN $s/p^{.62}$ AGAINST LOG TIME FOR RUNS 85 TO 90 AT CONSTANT VOLUME AND 25°C

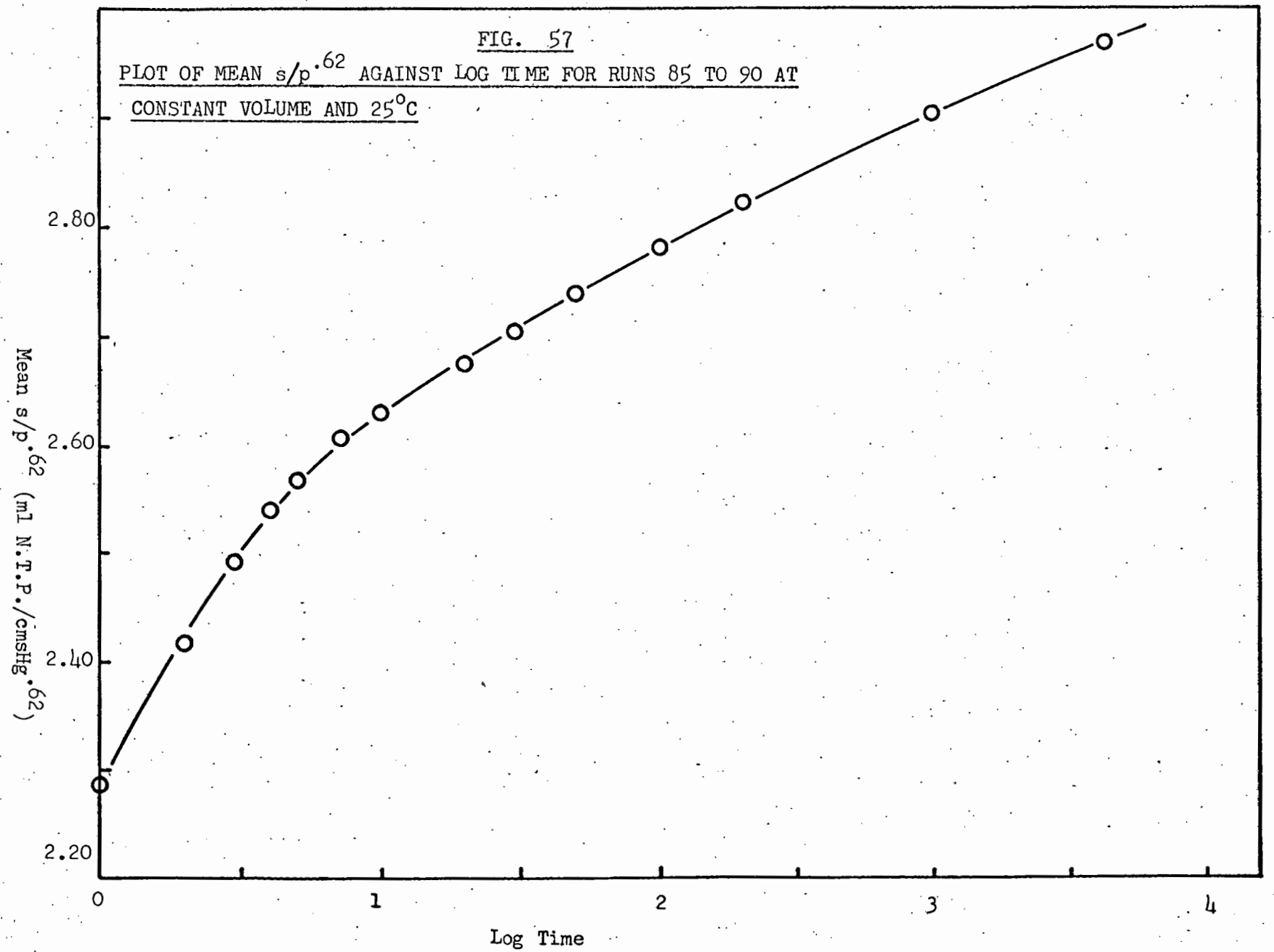


FIG. 58

PLOT OF $\frac{\Delta \text{MEAN } s/p^{.62}}{\Delta t}$ AGAINST MEAN $s/p^{.62}$ FOR RUNS 85 TO 90 AT CONSTANT VOLUME AND 25°C

Slope = -0.0915 (min^{-1}_{62})
Intercept at $\frac{\text{mean } s/p^{.62}}{t}$ = 0 = 2.706 (ml N.T.P./cmsHg$^{.72}$)
k = 1.22

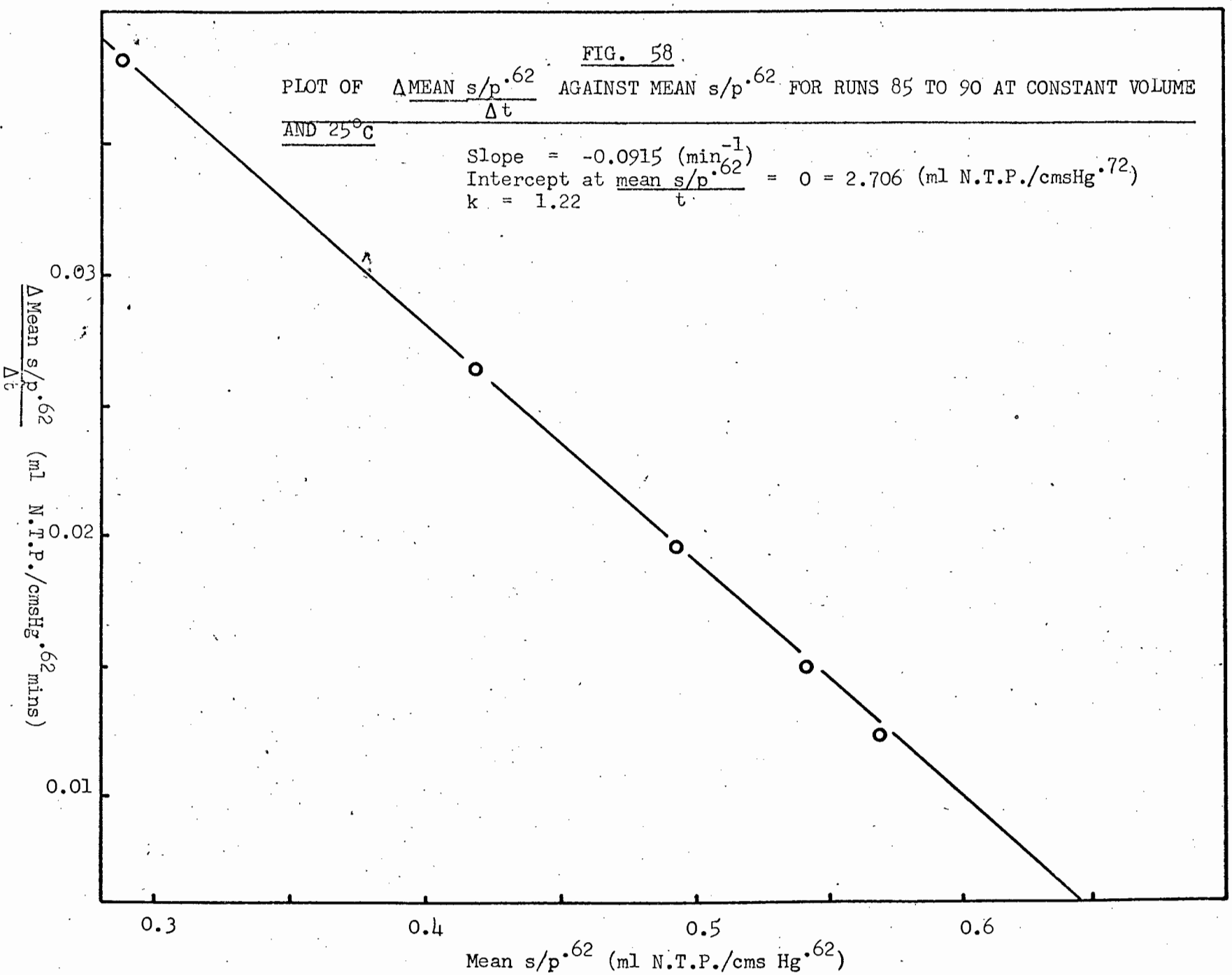


FIG. 59

PLOT OF $\frac{\Delta \text{MEAN } s/p^{.72}}{\Delta t}$ AGAINST MEAN $s/p^{.72}$ FOR RUNS 40 TO 60 AT CONSTANT PRESSURE AND 42.6°C

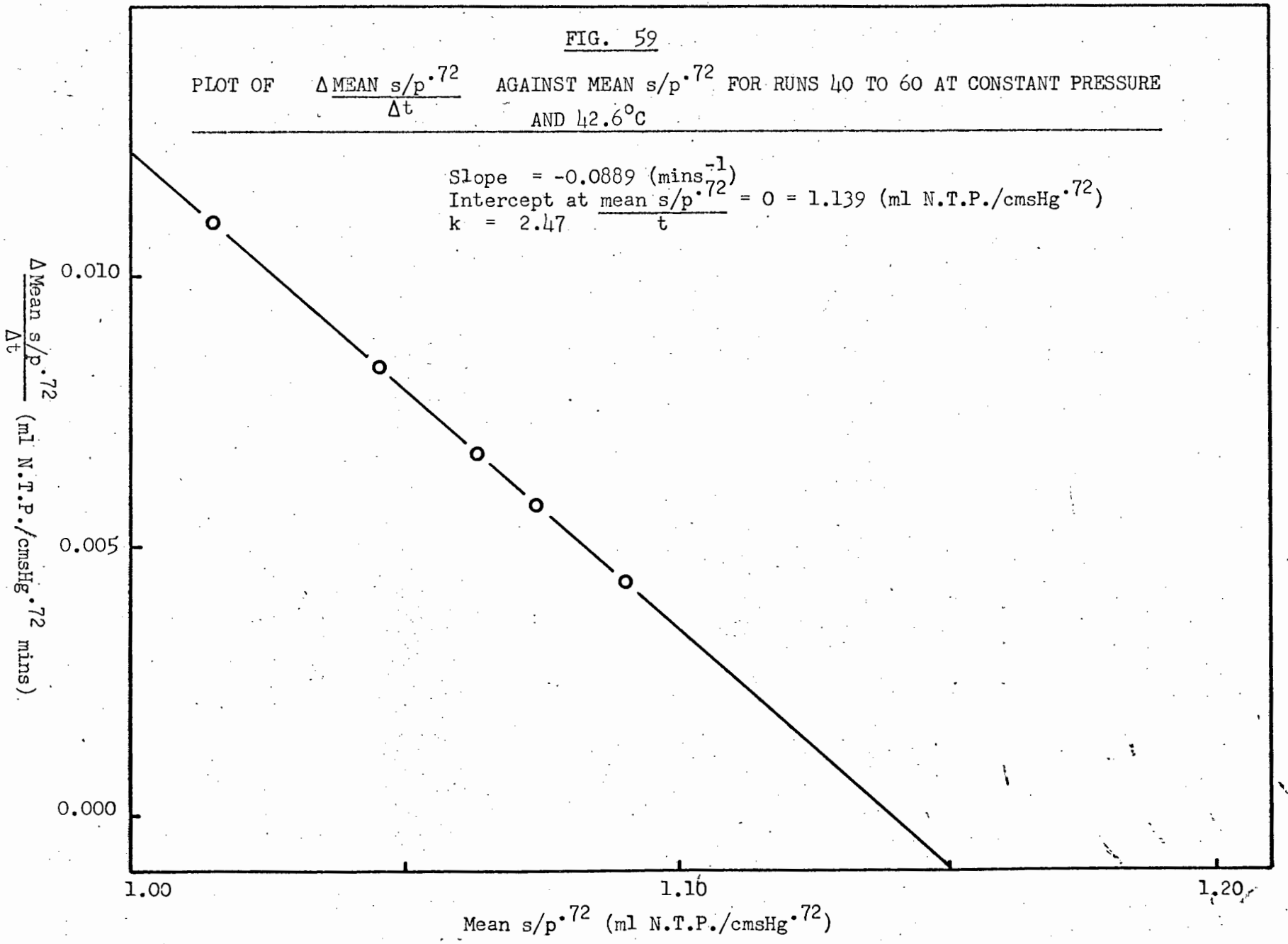


FIG. 60

PLOT OF (Mean $s/p^{.62}$ - (2.706 - $(1.22t + 1.12)^{-1}$)) AGAINST LOG TIME FOR RUNS 85 TO 90 AT CONSTANT VOLUME AT 25°C

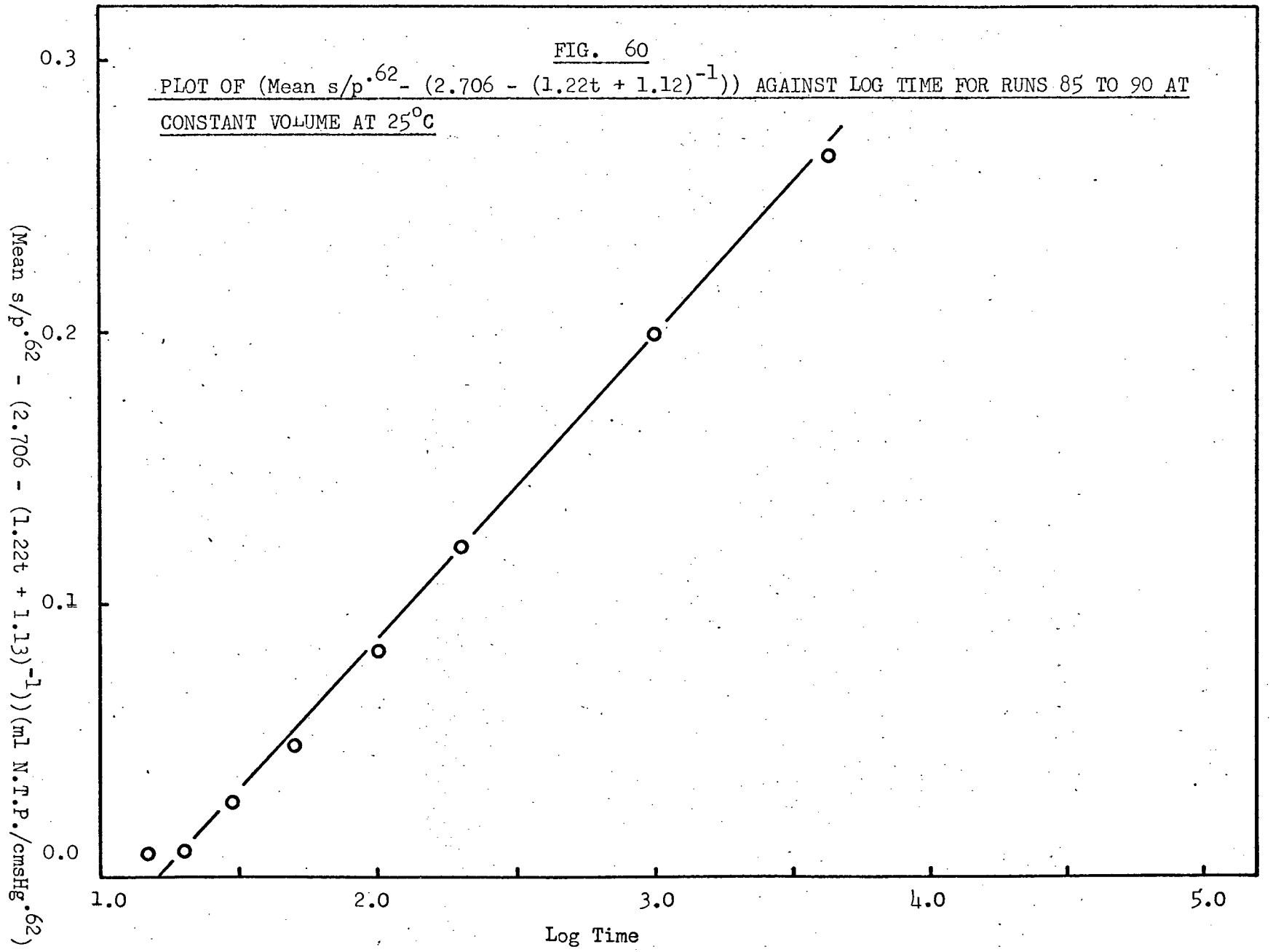
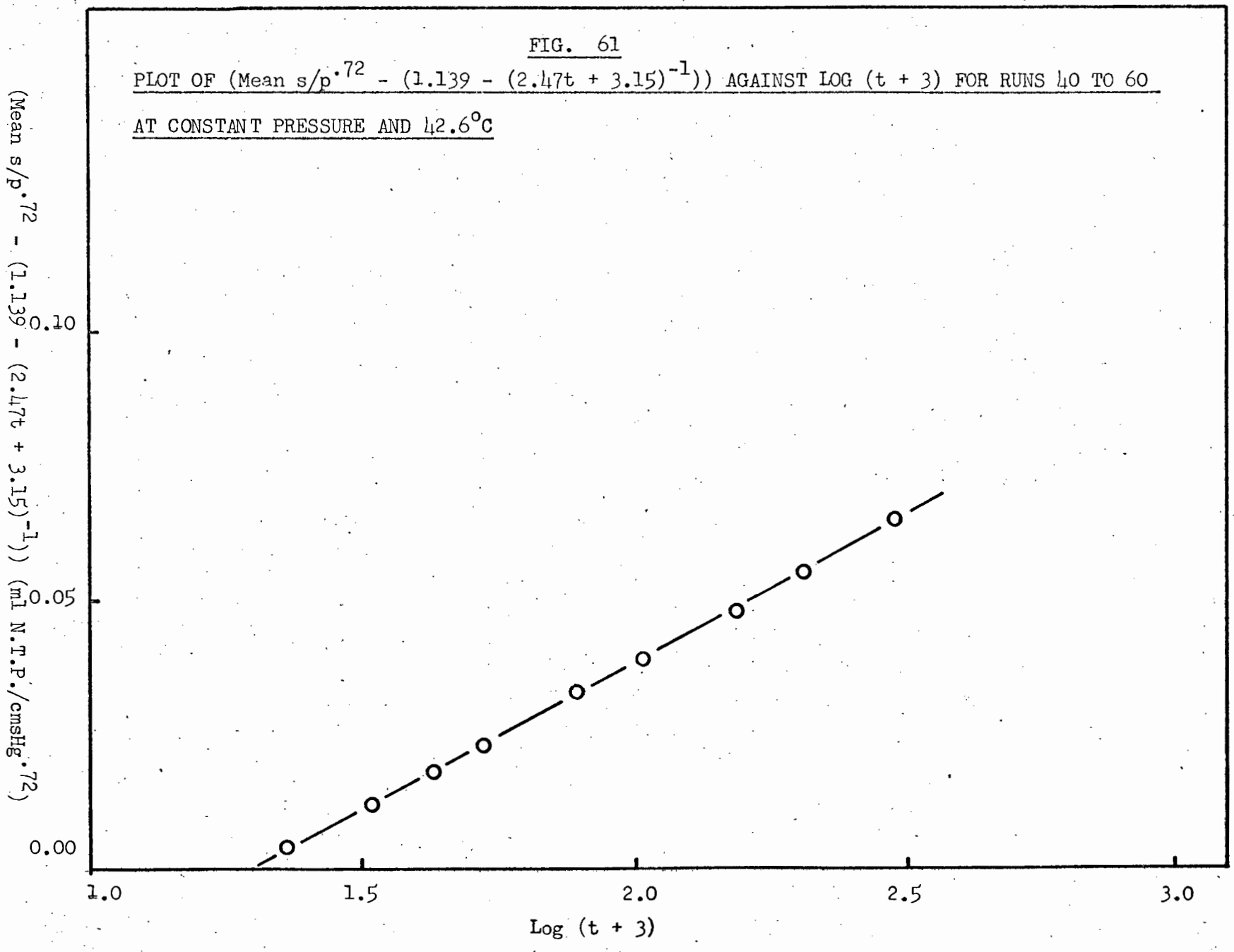


FIG. 61

PLOT OF (Mean $s/p^{.72}$ - (1.139 - $(2.47t + 3.15)^{-1}$)) AGAINST LOG (t + 3) FOR RUNS 40 TO 60 AT CONSTANT PRESSURE AND 42.6°C



amount adsorbed by the second process can be represented by the equations:

$$\left(\frac{s'}{p^{0.62}}\right)_{25^\circ C} = 0.112 \log (\tau_{25} + 16) - 0.112 \log 16$$

and

$$\left(\frac{s'}{p^{0.72}}\right)_{42.6} = 0.055 \log (\tau_{42.6} + 20) - 0.055 \log 20$$

in which $\tau_{25} = t - 16$ and $\tau_{42.6} = t - 17$ and s' = amount adsorbed by this process. The overall amounts adsorbed when both slow processes are operating can thus be calculated from the relationships:

$$\left(\frac{s}{p^{.72}}\right)_{42.6^\circ C} = 1.139 - \frac{1}{2.47t+3.15} + 0.055 \log (\tau_{42.6} + 20) - 0.055 \log 20$$

$$(t \geqslant 17 \text{ mins})$$

$$\left(\frac{s}{p^{.62}}\right)_{25^\circ C} = 2.706 - \frac{1}{1.22t+1.13} + 0.112 \log (\tau_{25} + 16) - 0.112 \log 16$$

$$(t \geqslant 16 \text{ mins})$$

4.7 Test of the equations.

The equations were tested by using them to calculate values of $\left(\frac{s}{p^m}\right)_T$ and then comparing these calculated values with the observed values of Tables 9 and 10. The good agreement that exists between the calculated and observed values of $\left(\frac{s}{p^m}\right)_T$ is shown in Table 11.

Further tests were performed by comparing calculated values of the amounts adsorbed with those actually observed in two experiments. It was realised, that as the parameters of the theoretical equations were determined from mean values of $\left(\frac{s}{p^m}\right)_T$, these mean values being obtained from individual runs, between which there was a fair amount of scatter, the fit to any run chosen at random would not be exact. The best that could be hoped for was that the equations would describe the course of the run qualitatively and that the difference between calculated and observed amounts would always differ by an approximately constant amount.

TABLE 11.

Comparison of observed and calculated values of $(\frac{s}{p^m})_T$

Time (mins)	T = 42.6°C		T = 25.0°C	
	Observed value	Calculated value	Observed value	Calculated value
1	-	-	2.287	2.280
2	1.015	1.015	2.419	2.426
3	1.045	1.044	2.453	2.497
4	1.063	1.062	2.541	2.540
5	1.074	1.074	2.569	2.568
7	1.090	1.090	2.608	2.603
10	1.103	1.103	2.631	2.631
15	1.116	1.114	2.663	2.655
20	1.124	1.123	2.675	2.678
30	1.138	1.138	2.707	2.709
40	1.147	1.147	-	-
50	1.154	1.154	2.739	2.745
75	1.166	1.167	-	-
100	1.174	1.174	2.782	2.787
150	1.184	1.185	-	-
200	1.192	1.192	2.824	2.825
300	1.203	1.199	-	-
1000	-	-	2.905	2.906
4300	-	-	2.971	2.978

The two runs chosen for comparison with the amounts calculated from the equations were: Run 60 at constant pressure and 42.6°C and Run 78 at 25°C. In this latter run the conditions under which the run was performed were changed from those of constant pressure to those of constant volume after 71 minutes, the observed s against log t plot for this run showing a break in the curve at this point. (Fig. 34).

Numerical comparison between s calculated and s observed are shown in Tables 12 and 13 and graphical comparison in Figures 62 and 63. The figures in the last columns of Tables 12 and 13 indicate that there is an approximately constant difference between observed and calculated values. The graphical comparisons show that the observed and calculated plots are qualitatively similar.

FIG. 62

COMPARISON OF s(calc) and s(obs) FOR RUN 60 AT 42.6°C

● = Calculated amount
○ = Observed amount

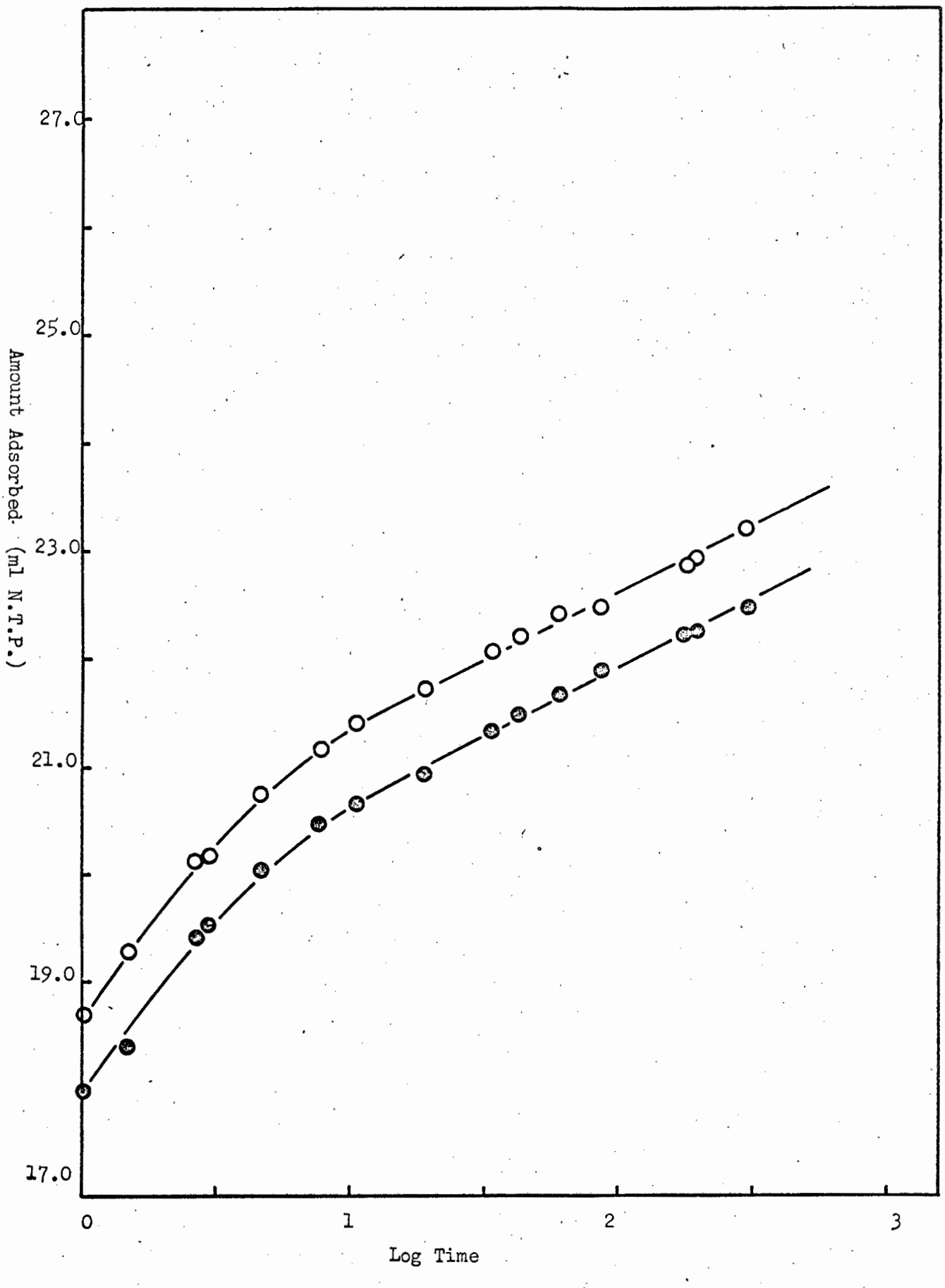


FIG. 63

COMPARISON OF s(calc) and s(obs) FOR RUN 78 AT 25°C.

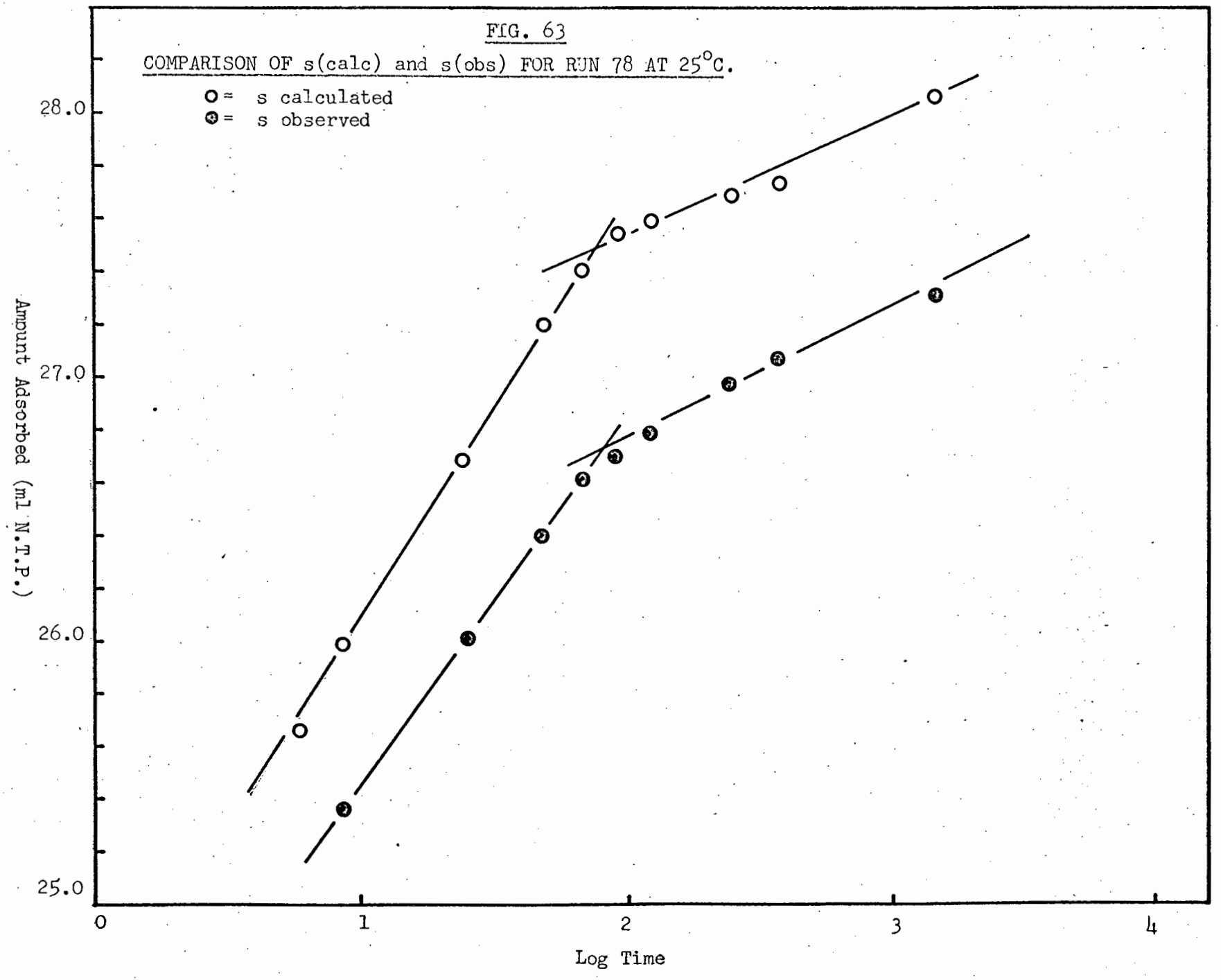


TABLE 12.

Comparison of s observed with s calculated for run 60 at 42.6°C.

Time	s observed	s calculated	$s_{obs} - s_{calc}$
(mins.)	(ml N.T.P.)	(ml N.T.P.)	(ml N.T.P.)
0.6	17.91	17.22	0.69
1.0	18.66	17.97	0.69
1.5	19.28	18.38	0.90
2.8	20.12	19.41	0.71
3.0	20.18	19.54	0.64
4.8	20.75	20.05	0.70
7.8	21.16	20.46	0.70
10.7	21.41	20.66	0.75
19.3	21.72	20.93	0.79
33.8	22.09	21.34	0.75
43.0	22.21	21.49	0.72
60.2	22.41	21.67	0.74
87.0	22.47	21.86	0.61
180.0	22.86	22.23	0.63
196.0	22.93	22.25	0.68
300.0	23.23	22.48	0.75

TABLE 13.

Comparison of s observed and s calculated for run 78 at 25°C.

Time	s observed	s calculated	$s_{obs} - s_{calc}$
(mins.)	(ml N.T.P.)	(ml N.T.P.)	(ml N.T.P.)
0.9	21.78	22.43	-0.65
1.5	22.69	23.48	-0.79
1.9	23.31	23.97	-0.66
2.7	23.73	24.57	-0.84
3.3	24.41	24.92	-0.51
6.0	24.99	25.66	-0.67
8.8	25.36	25.99	-0.63
23.8	26.00	26.69	-0.69
48.3	26.40	27.20	-0.80
66.6	26.62	27.40	-0.78
90.0	26.71	27.55	-0.84
120.0	26.79	27.59	-0.80
240.0	26.98	27.69	-0.71
361.0	27.07	27.73	-0.66
1440.0	27.31	28.07	-0.76

CHAPTER 5.

Discussion and Conclusions.

5.1 The adsorption isotherms of vinyl chloride on polyvinyl chloride.

Because of the occurrence of a slow uptake of monomer, determination of adsorption isotherms involved a lengthy procedure of doubtful precision. The procedure adopted was to allow a small aliquot of monomer to remain in contact with the previously evacuated polymer for 48 hours at constant temperature and to assume that equilibrium was established within this period. A further aliquot of monomer was then added to the now partially covered surface and the system again allowed to stand for 48 hours to equilibrate. This procedure was repeated for further doses of gaseous monomer until the desired pressure range had been covered.

The assumption that equilibrium would be established after 48 hours was rather arbitrary and at higher pressures definitely not true. When the system was allowed to stand under pressures of the order of 400 mm Hg or more the pressure continued to fall slowly after the 48 hours had elapsed. It was also observed that if large aliquots were added the amount adsorbed after 48 hours, at a particular pressure, was smaller than that adsorbed when the same pressure was arrived at via smaller aliquots.

The uncertainty as to the nature of the slow process also detracts from the significance of the isotherms. If the slow process is a slow adsorption then the amount of monomer taken up by it should be included in the overall isotherm. On the other hand, if the slow process is due to absorption, then the amount taken up by it should be subtracted from the total amount taken up at equilibrium, to give the true adsorption isotherm.

A tentative conclusion as to the nature of the slow process might be drawn from the isotherms. At the lower pressures (< 30 torr) equilibrium is apparently established within 10 minutes, the slow drift towards equilibrium only occurring at higher pressures. At pressures higher

than 200 torr the amount of monomer taken up exceeded the volume of krypton necessary to form a monolayer on the surface of the adsorbent.

The slow process accounted for about 10% of the total monomer adsorbed, the other 90% being adsorbed within the first minute of the reaction. At pressures greater than 200 torr this 90% was more than sufficient to give a monolayer on the surface. This must mean that for the higher layers, at least, the adsorption was of a physical nature. Also the rapid initial adsorption indicated that on a freely available surface no activation energy was required. The slow process was therefore probably due to some form of incorporation in the polymer. This incorporation could take the form of adsorption on internal surfaces produced by adsorption swelling for example, or it could be due to solution in the polymer. Incorporation of the monomer in the polymer would also account for the observed hysteresis in the isotherms.

The isosteric heat of adsorption, calculated from the overall isotherms, could only give a very rough estimate of the true heat of adsorption, because of the thermodynamic irreversibility of the isotherm and because equilibrium had not been completely established. For the range of pressure, over which the isotherms were measured, these approximate heats of adsorption fell linearly with the logarithm of amount adsorbed (Fig. 11) ranging from 9.5 k cal/mole at the lowest pressure at which measurements were made to 6 k cal/mole at the highest pressure. The measurements were made at temperatures below the critical temperature of the monomer and as the molar heat of vapourisation of vinyl chloride at its boiling point, (-13.9°C at 1 atm pressure) is 5.5 k cal/mole[85] no decision could be taken as to whether the adsorption of the first layer on the surface was physical or chemisorption.

In spite of the doubtful nature of the experimentally obtained

isotherms they did show certain interesting characteristics. Mathematically they were best represented over the pressure range of the experiments by Freundlich plots (Fig. 9 and Fig. 64). The actual log-log plots might be slightly curved (Fig.64) but the curvature was very small. This apparent obedience to the Freundlich isotherm may be more than coincidence because, (a) the isosteric heats calculated from the isotherms show the correct dependence on surface coverage (Fig. 11) and (b) the slopes of the Freundlich plots for these isotherms increases linearly with temperature (Fig. 65) as demanded by theory. There was also a certain degree of reproducibility. The slope of the log-log plot for the isotherm at 25°C determined in section 2 was almost identical with the value obtained at 25°C in section 3 using a different apparatus and a much larger polymer sample. However, the slope for the isotherm at 42°C, determined in section 3, was lower than would be expected from the results of section 2 (Fig. 65).

Reproducibility of isotherms was also fair as can be seen from the points plotted for Runs 67 and 69 at 42°C in Figure 64. However, it must be stressed that this reproducibility was only obtained provided that the procedure adopted to obtain the isotherm, including the size of the aliquots, was the same.

The Freundlich isotherm is a Type I isotherm, i.e., it represents the formation of a monolayer on the surface. The obedience of the "vinyl chloride adsorbed on polyvinyl chloride" system, in which the amounts adsorbed indicated that more than a monolayer was formed; to this type of adsorption isotherm, is surprising.

5.2 The rate of monomer adsorption in the vinyl chloride adsorbed on polyvinyl chloride system.

When the monomer was allowed to come into contact with the

FIG. 64

FREUNDLICH PLOTS FOR RUN 76 AT 25°C AND RUNS 67 AND 69 AT 42°C

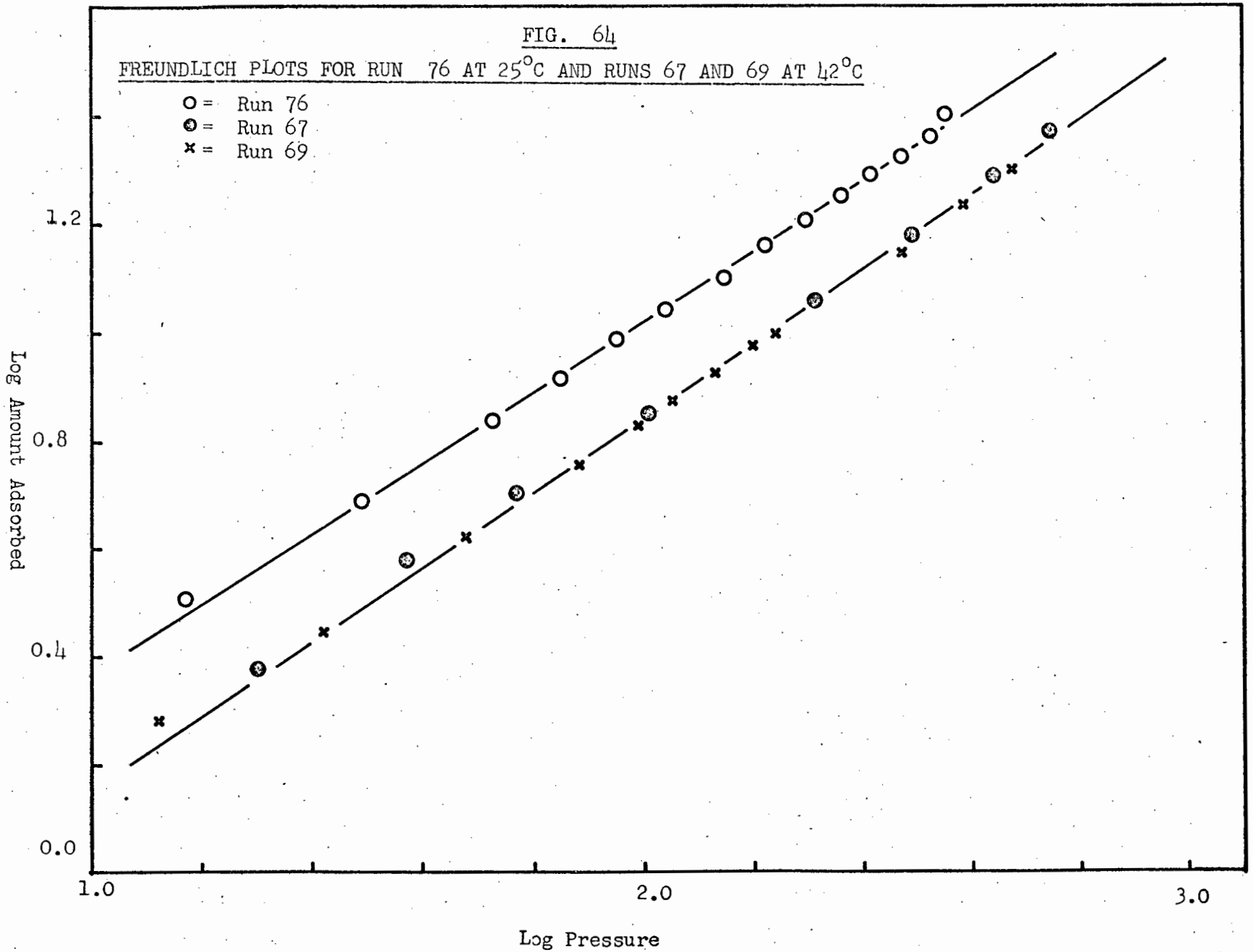
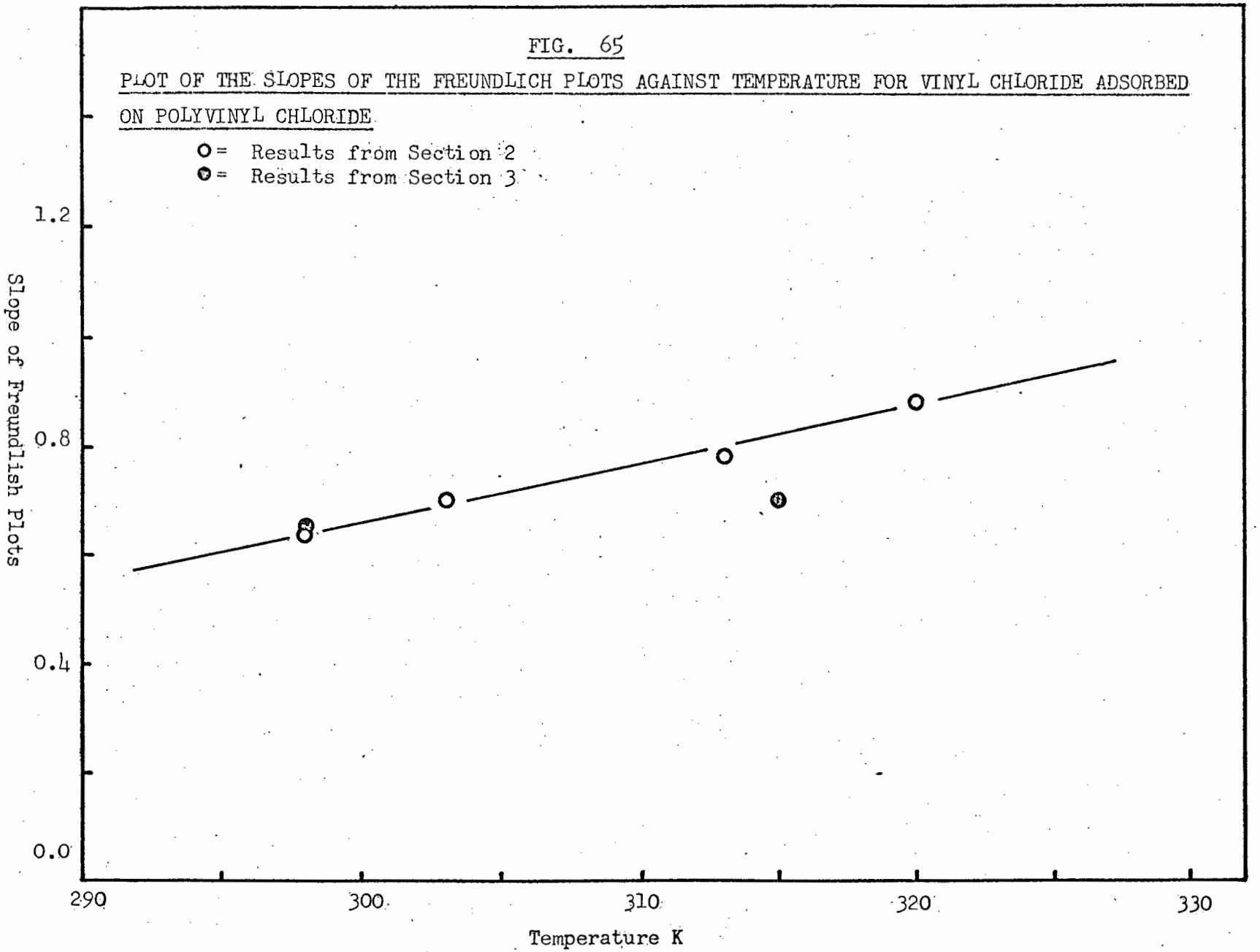


FIG. 65

PLOT OF THE SLOPES OF THE FREUNDLICH PLOTS AGAINST TEMPERATURE FOR VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE



freshly evacuated polymer, a rapid instantaneous takeup of monomer occurred. The rapid takeup of monomer was followed by a slow takeup of monomer. This slow process, at pressures of 500 - 600 torr, had been followed for periods up to 10 days without establishment of equilibrium. At lower pressures (< 100 torr) equilibrium was apparently established within 72 hours. At still lower pressures (< 30 torr) equilibrium was apparently established within 10 minutes. The rapid adsorption accounts for between 80 - 90% of the total amount adsorbed. The rate of the slow process decreased steadily during the course of a run.

Increasing the pressure suddenly during the course of a run resulted in an instantaneous increase in the amount of monomer taken up, followed by a slow increase in monomer takeup (Figs. 26 and 37). A sudden decrease in pressure resulted in an instantaneous desorption of monomer, followed by a slow takeup of monomer, if the pressure decrease occurs within the first ten minutes after the commencement of the run (Fig. 27). If the pressure decrease occurs at times greater than 20 hours after the start of the run, the instantaneous desorption is followed by a slow desorption and not by further takeup of monomer (Figs. 28 and 29). The slow process which follows a sudden increase in pressure is slower than would be observed if an aliquot of monomer, equivalent to the pressure increase, was added to a freshly evacuated surface. This indicates that the monomer already adsorbed causes a retardation in the rate.

The slow up take of monomer, which followed a pressure decrease within the first ten minutes of the reaction, indicated that the instantaneous adsorption and the slow up take were two different processes. The slow desorption which followed a pressure decrease after 20 hours indicated that the slow process could reach equilibrium at a given pressure if the run was continued for a long enough period.

5.2.1 The instantaneous process:

In section 3.2.3 two experiments were described. The results obtained from these experiments showed that the instantaneous process was reversible. In the first experiment, the pressure in the system was increased and then decreased stepwise over a period of time, short enough for the amount adsorbed or desorbed by the slow process to be considered negligible. After each increase or decrease in pressure, the amount adsorbed was calculated and plotted against the pressure (Fig.30). Over the short pressure range of the experiment the plot appeared to be linear with slope 0.024 ml/torr with the desorption and adsorption points lying on the same curve. In the second experiment the pressure was increased at 24 hour intervals by adding a small aliquot of monomer to the system. Immediately after the addition of the aliquot the amount adsorbed was calculated and the extra amount adsorbed because of the pressure increase was then divided by the increase in pressure. These results were tabulated as $\frac{\Delta s}{\Delta p}$ in Table 3. Examination of the tabulated values of $\frac{\Delta s}{\Delta p}$ showed that this ratio decreased as the pressure increased but the good agreement between the value of $\frac{\Delta s}{\Delta p}$ and the value of 0.024 ml/torr obtained in the first experiment over the same pressure range, confirmed the validity of the result obtained in the first experiment.

At the higher pressures the amount adsorbed by the instantaneous process was greater than the volume of krypton required to form a monolayer on the surface. The instantaneous adsorption seemed therefore to be multimolecular and probably of a physical nature. However, the possibility that the surface might be covered with a chemisorbed monolayer, on which the higher layers were physically adsorbed, cannot be excluded. The very fast rate at which this adsorption occurred showed that it was non-activated or alternatively had a very low activation energy.

5.2.2 The slow process.

In section 4 it was shown that the slow process was actually two processes. There was a process which commenced at the beginning of the run and proceeded throughout the whole period of the run. At constant pressure this process obeyed the rate equation $\frac{ds}{dt} = \frac{k}{p^m}(s_\infty - s_t)^2$ where s_∞ was the equilibrium amount adsorbed by this process and the instantaneous process alone, and k was a temperature dependent constant. It was also shown in section 4 that both s_∞ and s_t were proportional to p^m so that the rate equation at constant pressure had the form

$$\frac{ds}{dt} = k'p^m(1 - \theta)^2 \quad \text{where } \theta = \frac{s_t}{s_\infty}.$$

The second process commenced some time (approximately 10 minutes) after the start of the run and this process at constant pressure obeyed a rate law of the form

$$\frac{ds}{dt} = ap^m e^{\frac{-\alpha s}{p^m}}$$

In this equation a was a constant at constant temperature, s was the amount adsorbed by the process and α was of the form

$$\alpha = C(T)$$

In some respects the "vinyl chloride on polyvinyl chloride" system (System I) resembled the "oxygen adsorbed on cuprous oxide" system (System II).[67] They are similar in as much as:

(i) In both systems more adsorbate was taken up than would be required to form a monolayer on the surface.

(ii) In both systems there was a slow takeup of adsorbate and this slow process could be divided into two processes, the first of which started at the commencement of the adsorption and had a rate equation of the form $\frac{ds}{dt} = kf(p)(1-\theta)^2$. The second process in both systems started at some time after the commencement of the adsorption and obeyed a rate equation of the Elovich type.

(iii) In System II the rate of the first slow process was proportional to "p" the pressure at all temperatures. In System I the rate of the first slow process was proportional to "p^m" where "m" is a constant at constant temperature. "m" had a value less than unity and decreased as the temperature decreased.

(iv) In System II when the first slow process only was occurring a plot of $\frac{1}{s_n - s_t}$ against time at constant pressure was linear. s_n was the amount adsorbed to cover the surface with a monolayer. The slopes of these plots were found to be proportional to the pressure at which they were measured. In System I a plot of $\frac{1}{s_\infty - s_t}$ against time was linear at constant pressure but the slope of the plot was inversely proportional to p^m.

(v) In System II the rate of the second slow process was proportional to the pressure. The rate equation for this process was of the form $ape^{-\alpha s}$ where a and α were constants at constant temperature. In System I the rate equation for the second process was of the form $ap^m e^{\frac{-\alpha s}{p^m}}$ where a and α were constants at constant temperature. In System II α decreased with increasing temperature but in System I α appeared to increase with increasing temperature.

The fact that the rate of the slow processes in System I was proportional to p^m and not proportional to p, as in System II, suggested that these processes were dependent on monomer already adsorbed on the surface when they commenced.

The second slow process in System I could still be an incorporation of monomer in the polymer. This incorporation could arise because of diffusion of monomer from the surface layers to new areas produced in the polymer on which further adsorption could occur. As the second slow

process only occurred some time after the start of the reaction it would follow that these new areas only became effective at a later stage in the reaction. If adsorption on these new areas occurred with a linearily increasing activation energy an Elovich type rate equation would be obeyed. The dependence of the exponent of "e" in this equation, on the reciprocal of p^m, suggested that at higher pressures, and therefore at higher amounts adsorbed on the external surface, the internal surface would be more accessible, i.e., the activation energy increased more slowly.

5.2.2.1 The dependence of the amount adsorbed at a given time on the pressure.

It was shown in section 4.4 that the amount adsorbed at a given time was proportional to p^m, i.e., $s_t = a_t p_t^m$ where a_t is a constant for a given value of t, the time, at constant temperature. This relationship held for runs performed under constant pressure and constant volume conditions provided that the run was started on a freshly evacuated surface and that there were no sudden increases or decreases in pressure during the course of the run.

A sudden increase of pressure during the course of a run resulted in the ratio $\frac{s_t}{p_t^m}$ being less than a_t for an uninterrupted run. A sudden decrease in pressure resulted in $\frac{s_t}{p_t^m}$ being greater than a_t for an uninterrupted run. The gradual pressure decrease, which occurred during the course of a run at constant volume, caused no deviation from the above relationship. A change from conditions of constant pressure to conditions of constant volume, or a reduction of the volume of the system, without altering the pressure during the course of a run at constant volume, also caused no deviation from the above relationship.

If the pressure is increased suddenly during the course of a run new sites will be created by the extra amount rapidly adsorbed. At a given time, therefore, after the increase in pressure the extent of slow reaction, measured in terms of the total number of sites which had been created, will be less than it would have been, had the extra sites been present from the beginning of the reaction. As a result $\frac{s_t}{p^m}$ will be less than a_t for an uninterrupted run.

Conversely if the pressure is suddenly decreased there is an instantaneous desorption which should result in a decrease in the number of sites. However, if sites which should disappear are already covered there will be a delay while desorption from these sites occur. Consequently, more monomer will be adsorbed than should be at the lower pressure and $\frac{s_t}{p^m}$ will be greater than a_t.

If the pressure drops gradually, as under constant volume conditions, the sites which disappear are unoccupied and hence the number of sites decrease but the surface area covered also decreases and hence the site concentration remains constant.

5.2.2.2 A mechanism for the first slow process.

The occurrence and the observed kinetics of this process could be explained in terms of the mechanism proposed in Section 5.2.2.1 and rearrangement of the spontaneously adsorbed monomer on the surface.

It can be supposed that at a given pressure, if the adsorbate molecules are packed on the surface in a systematic fashion, each molecule occupying two adjacent sites, the maximum utilisation of adsorption sites will occur and the maximum amount s_∞ at the given pressure will be adsorbed. Howevever, if the initial adsorption is random then certain sites will be excluded as there will not necessarily be a second site with the correct

spacing for adsorption in the vicinity. If rearrangement of the adsorbed molecules now occurs on the surface, then during the course of this rearrangement a vacant site can come into contact with a second vacant site. If the rate of adsorption of a molecule from the gaseous phase on to a pair of adjacent sites is rapid then the rate of the slow process will depend on the rate at which the vacant sites collide.

If the arguments of the previous section are now applied to these sites then the concentration of these sites at any time will be proportional to $\frac{s_\infty - s_t}{p^m}$.

Hence the rate of collision of these sites and hence the rate of the slow process will be given by

$$-\frac{d\left(\frac{s_\infty - s_t}{p^m}\right)}{dt} = k\left(\frac{s_\infty - s_t}{p^m}\right)^2$$

at constant pressure this reduces to:

$$\frac{ds}{dt} = \frac{k}{p^m}(s_\infty - s_t)^2$$

which is the observed rate law.

5.2.2.3 A mechanism for the second slow process.

This process which commences some ten minutes or so after the start of the reaction has a rate equation of the form

$$\frac{ds}{dt} = ap^m e^{\frac{-\alpha s}{p^m}}$$

where α is a constant at constant temperature and m has the same value as in the first process. The late appearance of this process suggests that if it is an adsorption process, there is some delay in the formation of the adsorption sites on which it occurs. The appearance of the p^m term in the rate expression suggests that the process is dependent on the amount of monomer previously adsorbed. This last hypothesis is supported by the observation that at pressures below 30 mm Hg equilibrium is apparently

established within 10 minutes, the very slow process being undetectable with the apparatus used.

New areas for adsorption can be created within the polymer if adsorption swelling occurs.[55,86] This phenomonen, which results because of the amount adsorbed on the surface, causes distortion of the polymer structure and this distortion may cause it to spring open at various points to expose new areas. This distortion and opening of the interior areas of the polymer may take time and this will account for the late start of the process. At very low pressures the distortion of the polymer structure may not be sufficient for the new areas to be exposed and hence the slow process does not occur.

Once the new areas have been exposed diffusion to these areas from the monomer adsorbed on the surface can occur. The monomer, which is adsorbed on the new areas, could cause further distortion of the polymer and thereby create further sites for adsorption. If these sites are created with a linearily increasing activation energy, an Elovich type rate equation will result. At higher pressures there is greater distortion of the surface and hence new areas are more easily produced at higher pressures than at lower pressures. This could mean that the increase of activation energy for the production of new sites is less at higher pressures than at lower pressures and this would account for the $\frac{"\alpha"}{p^m}$ term in the above rate equation. The occurrence of adsorption swelling will also account for the observed hysteresis[86] in the adsorption isotherm.

5.3 The role of the polymer in the polymerisation of vinyl chloride.

In the Bengough and Norrish mechanism[3] for the polymerisation of vinyl chloride it was supposed that chain transfer took place between a growing radical and dead polymer. Instinctively it would be thought

that the molecular mass of the polymer should thus increase with time whereas experimentally it was found that the molecular mass remained constant.

As adsorption of monomer on the polymer has been shown to take place, it is more likely that chain transfer takes place between adsorbed molecules on the surface and growing free radicals from the bulk liquid phase rather than between the polymer and the growing free radical. These new radicals will continue to grow as they are surrounded by an ordered array of correctly aligned adsorbed monomer molecules until they are terminated by chain transfer with monomer from the bulk liquid phase.

5.4 The vinylidene chloride - polyvinylidene chloride system.

For the reasons stated in section 2, not many measurements were made on this system. The few measurements that were made indicated that the system behaved similarly to the vinyl chloride-polyvinyl chloride system. However, the reproducibility of measurement was so poor that no quantitative verification of this statement was possible.

5.5 Conclusions.

Adsorption of monomer on polymer occurs in both the vinyl chloride adsorbed on polyvinyl chloride and vinylidene chloride adsorbed on polyvinylidene chloride systems. In both systems there is a rapid initial adsorption followed by a much slower process. The amount rapidly adsorbed seems to be greater for the vinyl chloride system than for the vinylidene chloride system but the quality of the measurements made on the latter system were very poor and no conclusions could be drawn from them. Effort was therefore concentrated on the vinyl chloride system.

Kinetic measurements were made on this system at two temperatures

namely 25°C and 42.6°C. It was shown that the rapid initial adsorption was reversible with respect to pressure and that at higher pressures the amount adsorbed could exceed a monolayer. The slow process which followed the initial rapid process was shown to consist of two processes. The first of these occurred from the beginning of the reaction and obeyed a rate law of the form $\frac{ds_t}{dt} = \frac{k}{p^m}(s_\infty - s)^2$. The second process started later in the reaction and was shown to obey an Elovich type rate equation. A mechanism in terms of surface rearrangement was put forward to account for the first slow process and a mechanism based on adsorption swelling was put forward to account for the second slow process.

Measurement of adsorption isotherms was complicated by the slow process which, at higher pressures, approached equilibrium exceedingly slowly. The isotherms obtained were thus of rather poor reproducibility and desorption experiments showed that they exhibited hystereisis. However, the adsorption branches of the isotherms obeyed Freundlich plots over most of their range, and the isosteric heats calculated from these plots showed the correct theoretical dependence on surface coverage. The values obtained for the isosteric heats of adsorption are in doubt because the isotherms are not thermodynamically reversible. The values obtained for these approximate heats of adsorption, taken together with the fact that the system seemed to exhibit multimolecular adsorption, suggested that the adsorption was of the van der Waal's type.

In view of the fact that adsorption does occur on the polymer surface, it is suggested that in the Bengough and Norrish mechanism for the polymerisation of the monomer chain transfer occurs between adsorbed monomer molecules on the surface and radicals from the liquid phase and not between "dead polymer" and radicals from the liquid phase.

5.6 Further experimentation.

5.6.1 The vinyl chloride on polyvinyl chloride system.

The first objective of any further research done on this system will have to be the improvement of reproducibility. The course of the research done in this thesis was plagued with leaks in the vacuum system. These leaks arose in some instances because of the use of poor quality stopcocks. The frequency with which leaks occurred meant that standardisation of the degassing procedure used was not always possible. The adsorbent was frequently exposed to the atmosphere when the stopcock isolating the reaction vessel from the rest of the system, had to be regreased.

It was observed in those instances in which it was possible to perform a set of runs without exposing the adsorbent to the atmosphere between runs, that under the same conditions of temperature and pressure, the amount of adsorbate adsorbed at a given time showed a tendency to increase from run to run. A suggested procedure for improving reproducibility is that after any exposure of the adsorbent to the atmosphere the adsorbent should be alternately saturated with adsorbate at the highest pressure in the range and then degassed. This cycle of saturating with adsorbate and then degassing to be continued until no regular increase in the amount adsorbed at a given time, under the same conditions of temperature and pressure, is observed.

The pressure range over which measurements were made should be extended below 30 torr. Below this pressure the very slow process does not seem to be significant and it is possible that reversible isotherms may be obtained in this region of the pressure range. If reversible isotherms can be obtained, reliable isosteric heats of adsorption can be

calculated. These isosteric heats would represent heats of adsorption at low coverages and their values might enable the type of adsorption occurring in the lowest layer to be elucidated. Also entropies of adsorption could be calculated and compared with theoretical entropy values and this would lead to some knowledge of the mobility of the adsorbed layers.

Measurements of rates of adsorption over a temperature range extending from the boiling point of the monomer up to 50°C should be made. This would enable the temperature variation of the parameters of the rate equations for the slow processes to be determined and hence make the calculation of activation energies for these processes possible.
If, as has been suggested, the hysteresis observed in the isotherms at higher pressures, is due to the second slow process, then a knowledge of the variation of the parameters of the rate equation for this process with pressure and temperature will enable isotherms to be calculated for the rapid initial process and the rearrangement process. These isotherms should be reversible and thus will make the calculation of isosteric heats of adsorption and entropies of adsorption possible for the higher pressures.

At the lower temperatures these isotherms will fall into the pressure range over which the B.E.T. equation is valid. It may thus be possible to obtain a value for the amount of monomer required to form a monolayer on the surface. Comparison of this amount with the amount of krypton required to form a monolayer on the surface, together with the use of scale models, could lead to some knowledge as to how the monomer molecules pack on the surface.

The mechanism put forward to account for the second slow process involved adsorption swelling. This should be tested for and if it is

found to occur, the variation of this phenomonen with amount adsorbed on the external surface and with pressure and temperature, should be examined.

5.6.2 The vinylidene chloride on polyvinylidene chloride system.

The major difficulties encountered with this system were:

(i) The polymer seemed to be unstable above 40°C.

(ii) The monomer was soluble to some extent in all stopcock greases.

(iii) The monomer tended to polymerise when exposed to light.

(iv) The monomer reacted with mercury, thus gas burettes and gauges containing mercury had to be avoided.

To avoid the use of stopcocks, it is suggested that a dilatometric method be used in the study of this system. Monomer can be sealed into a calibrated dilatometer kept at constant temperature. The gaseous monomer above the liquid monomer in the dilatometer will be at a constant pressure. This pressure will vary with the temperature of the dilatometer and can be measured by means of a membrane type gauge. The monomer can be brought into contact with the degassed polymer by breaking a glass seal which initially separates them. The amount of monomer adsorbed at any time can be calculated from the dilatometer readings and the dead space volume of the apparatus. To prevent polymerisation of the monomer the experiments can be performed in the dark (some light will be required to read the dilatometer) or the apparatus can be painted black. Decomposition of the polymer can be prevented by working at lower temperatures or by the addition of stabilisers, although the addition of stabilisers might alter the adsorption characteristics of the system.

APPENDIX 1.

CALIBRATION OF THE MONOMERS - DATA FOR FIGURES 2, 3 AND 4.

CALIBRATION OF APPARATUS FOR VINYL CHLORIDE REMOVAL. (Figure 2)

ROOM TEMPERATURE 19.2°C.

Initial Pressure p_1	Final Pressure p_2	Mass of Tube + monomer	Mass of empty tube	Mass of Monomer	$\Delta p = p_1 - p_2$
(torr)	(torr)	(g)	(g)	(g)	(torr)
666.8	493.0	9.427	9.139	0.288	173.8
493.0	314.0	10.509	10.208	0.301	179.0
314.0	152.2	9.232	8.971	0.261	161.8
152.2	3.0	9.432	9.198	0.234	149.2
128.3	5.0	9.570	9.375	0.195	123.3
202.7	5.2	9.480	9.164	0.316	197.5
306.0	4.9	9.555	9.064	0.491	307.1
506.3	3.1	10.211	9.383	0.828	503.2
59.6	2.4	9.169	9.073	0.096	57.2

CALIBRATION OF APPARATUS FOR VINYLIDENE CHLORIDE REMOVAL (FIGURE 2)

ROOM TEMPERATURE 21.5°C

Initial Pressure p_1	Final Pressure p_2	Mass of Tube + Monomer	Mass of empty tube	Mass of Monomer	$\Delta p = p_1 - p_2$
(torr)	(torr)	(g)	(g)	(g)	(torr)
306.5	46.0	10.596	9.536	1.060	260.5
204.0	46.0	8.005	7.400	0.605	158.0
121.0	44.0	7.888	7.597	0.291	77.0
162.0	46.0	9.025	8.593	0.432	116.0
242.0	54.0	8.316	7.585	0.731	188.0
264.0	48.0	7.908	7.055	0.853	216.0
82.0	26.0	7.378	7.175	0.203	56.0
280.0	52.0	8.756	7.810	0.946	228.0
277.0	50.0	9.514	8.575	0.939	227.0
182.0	48.0	8.968	8.442	0.526	134.0
146.0	44.0	8.616	8.228	0.388	102.0
236.0	56.0	9.262	8.531	0.731	180.0
109.0	48.0	8.404	8.181	0.223	61.0
293.0	62.0	9.163	8.186	0.977	231.0
297.0	109.0	9.197	8.420	0.777	188.0

EXTENT OF POLYMERISATION OF VINYL CHLORIDE (FIGURE 3)

TEMPERATURE 47°C

MOLE % INITIATOR 0.3

Time in thermostat	Initial Mass of Monomer taken	Mass of Monomer remaining	Mass of Polymer formed	% polymerisation
(hours)	(g)	(g)	(g)	(%)
6.0	0.200	0.189	0.011	5.4
10.5	0.200	0.177	0.023	11.5
12.0	0.200	0.171	0.029	14.8
15.0	0.200	0.164	0.036	17.9
18.0	0.200	0.160	0.040	20.3
20.0	0.203	0.158	0.045	22.6
24.0	0.200	0.142	0.058	29.0

EXTENT OF POLYMERISATION OF VINYL CHLORIDE (FIGURE 3)

TEMPERATURE 42°C

MOLE % INITIATOR 4.0%.

Time in thermostat	Initial Mass of Monomer taken	Mass of Monomer remaining	Mass of Polymer formed	% polymerisation
(hours)	(g)	(g)	(g)	(%)
2.0	0.503	0.430	0.073	14.5
4.0	0.502	0.322	0.180	35.9
6.0	0.503	0.112	0.391	77.7
8.0	0.503	0.090	0.413	82.1
10.0	0.504	0.064	0.440	87.3
16.5	0.501	0.048	0.453	90.4
20.0	0.503	0.044	0.459	91.2
24.0	0.502	0.033	0.469	93.4

EXTENT OF POLYMERISATION OF VINYLIDENE CHLORIDE (FIGURE 4)

TEMPERATURE 49°C

MOLE % INITIATOR 0.3%

Time in thermostat	Initial Mass of Monomer taken	Mass of Monomer remaining	Mass of Polymer formed	% polymerisation
(hours)	(g)	(g)	(g)	(%)
1.0	0.630	0.607	0.023	3.7
2.0	0.640	0.568	0.072	11.3
4.0	0.660	0.522	0.138	20.9
6.5	0.650	0.479	0.171	26.3
7.0	0.660	0.506	0.154	23.3
15.3	0.650	0.358	0.292	44.9
29.0	0.660	0.173	0.487	73.8

APPENDIX 2.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE ADSORPTION ISOTHERMS

DATA FOR FIGURES 9, 38, 39 and 64.

PRELIMINARY STUDY RESULTS (FIGURE 9)

25°C		30°C		40°C		47°C	
Equilibrium Pressure	S	Equilibrium Pressure	S	Equilibrium Pressure	S	Equilibrium Pressure	S
(torr)	(ml NTP)	(torr)	(ml NTP)	(torr)	(ml NTP)	(torr)	(ml NTP)
23.8	1.68	37.0	1.71	39.9	1.31	16.2	0.42
64.3	3.22	114.0	4.07	94.6	2.52	58.1	1.48
156.3	5.53	214.1	6.10	158.8	3.97	131.2	2.52
272.7	8.33	327.0	8.24	263.0	5.67	236.3	4.26
390.3	10.66	365.6	9.04	309.3	6.69		

RUNS 67, 68 and 69 ADSORPTION AND DESORPTION AT 42°C

RUN 67 Adsorption		RUN 68 Desorption		RUN 69 Adsorption	
Equilibrium Pressure	S	Equilibrium Pressure	S	Equilibrium Pressure	S
(torr)	(ml NTP)	(torr)	(ml NTP)	(torr)	(ml NTP)
20.1	2.41	534.2	23.51	4.2	0.91
37.5	3.80	500.9	22.68	13.3	1.90
58.8	5.12	458.9	21.71	26.2	2.77
101.4	7.19	397.9	20.39	48.2	4.15
204.9	11.57	319.5	18.26	76.0	5.68
306.9	15.32	248.3	16.01	97.5	6.74
435.0	19.49	151.9	12.32	112.1	7.37
550.0	23.85	95.3	9.50	134.0	8.30
		58.3	6.74	157.4	9.28
		37.0	3.83	172.1	9.83
		28.0	2.45	205.1	11.14
				296.0	14.05
				387.0	17.14
				471.8	19.93
				559.6	23.01

RUN 76 at 25°C

RUN 76 Adsorption	
Equilibrium Pressure	S
(torr)	(ml NTP)
14.8	3.24
30.9	4.94
53.1	6.93
71.1	8.29
89.2	9.79
110.7	11.13
140.3	12.88
165.2	14.63
195.9	16.18
226.8	17.83
256.1	19.67
296.2	21.35
331.8	23.54
357.5	25.44

APPENDIX 3

ADSORPTION ISOTHERSM FOR THE ADSORPTION OF VINYLIDENE CHLORIDE ON POLYVINYL CHLORIDE.

DATA FOR FIGURE 13.

27.8°C		37.5°C		47.1°C	
Equilibrium Pressure	S	Equilibrium Pressure	S	Equilibrium Pressure	S
(torr)	(ml NTP)	(torr)	(ml NTP)	(torr)	(ml NTP)
20.4	2.10	24.8	1.65	28.9	1.26
41.4	3.13	47.7	2.53	54.9	1.86
75.6	4.97	84.8	3.89	94.4	2.99
100.0	5.94	112.8	4.76	124.3	3.65

APPENDIX 4.

ISOTHERM FOR KRYPTON ADSORBED ON POLYVINYL CHLORIDE AT LIQUID NITROGEN TEMPERATURE.

DATA FOR FIGURE 40.

Equilibrium Pressure p	S	$\frac{p}{p^o}$	$\frac{\frac{p}{p^o}}{S(1-\frac{p}{p^o})} \times 10^4$
(torr)	(per mole)		$(\text{per mole})^{-1}$
0.074	0.029	281.4	1.06
0.125	0.049	353.1	1.46
0.219	**0.086**	**468.1**	**2.01**
0.470	0.184	641.2	3.52

APPENDIX 5.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE.

RATE RUNS AT CONSTANT VOLUME ON A PARTIALLY COVERED SURFACE.

DATA FOR FIGURES 28 AND 29.

Run No. 23(b)			Run No. 71			Run No. 71 (contd.)		
Temp. 42.6°C			Temp. 42.6°C			Temp. 42.6°C		
Previous amount adsorbed 8.60 ml NTP			Previous amount adsorbed 20.16 ml NTP			Previous amount adsorbed 20.16 ml NTP		
Time	Pressure	S	Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
1.0	180.8	9.5	0.50	680.3	23.50	60.00	665.9	24.03
2.0	180.4	9.28	1.00	677.3	23.61	90.00	664.6	24.09
3.0	180.6	9.27	2.00	675.1	23.69	120.00	663.2	24.15
5.0	180.7	9.27	2.50	674.7	23.70	180.00	661.2	24.21
10.0	180.6	9.28	3.00	673.1	23.77	315.00	658.5	24.30
20.0	180.5	9.29	4.00	672.5	23.79	540.00	654.9	24.44
40.0	180.0	9.34	5.00	671.7	23.83	1260	648.4	24.66
60.0	180.0	9.35	6.00	671.5	23.84	1740	645.3	24.79
100	180.1	9.35	7.00	671.1	23.85	2700	641.1	24.97
160	179.6	9.39	10.00	670.7	23.86	3105	640.1	25.00
200	179.6	9.39	15.00	669.6	23.91	4080	636.8	25.13
320	178.6	9.44	20.00	669.0	23.93	4500	636.5	25.16
1440	176.5	9.61	30.00	667.7	23.96	5640	632.9	25.25
			45.00	666.9	24.01	8650	628.7	25.43

RUN NO. 74		
Temp. 42.6°C		
Previous amount adsorbed 14.80 ml NTP		
Time	Pressure	S
(min)	(torr)	(ml NTP)
1.00	370.8	16.57
2.00	368.8	16.62
3.00	368.6	16.63
5.00	367.0	16.67
7.00	366.8	16.69
10.00	366.9	16.68
15.00	366.0	16.70
20.00	365.4	16.73
30.00	365.1	16.73
60.00	364.8	16.74
120.00	363.1	16.78
180.00	362.5	16.81
1140	365.7	16.95
5580	349.1	17.16

APPENDIX 6.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE

DESORPTION FROM A PARTIALLY COVERED SURFACE.

DATA FOR FIGURES 28 and 29.

RUN NO 23(C)			RUN NO. 72		
Temp. 42.6°C			Temp. 42.6°C		
Amount initially on surface 9.61 ml NTP			Amount initially on surface 25.43 ml NTP		
Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
1.0	136.0	8.59	1.00	232.9	17.91
5.0	136.4	8.54	2.00	237.9	17.78
10.0	136.4	8.54	3.00	240.1	17.73
20.0	136.2	8.55	4.00	242.1	17.68
40.0	136.4	8.53	5.00	242.7	17.67
100	-	-	6.00	243.1	17.66
200	136.9	8.47	7.00	243.5	17.66
300	136.8	8.48	10.00	244.9	17.62
1440	137.1	8.45	15.00	246.2	17.59
			20.00	247.0	17.57
			30.00	248.5	17.53
			45.00	250.0	17.49
			60.00	251.4	17.47
			90.00	252.8	17.43
			120.00	254.2	17.39
			180.00	256.2	17.35
			390.00	260.4	17.24
			1140	267.9	17.06
			2760	274.6	16.89
			5460	280.6	16.74

APPENDIX 7.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE

SUDDEN INCREASES OR DECREASES IN PRESSURE DURING THE COURSE OF A RUN AT 42.6°C.

DATA FOR FIGURES 26, 27 and 37.

RUN NO. 24			RUN NO. 25			RUN NO. 29		
Temp. 42.6°C			Temp. 42.6°C			Temp. 42.6°C		
Time (min)	Pressure (torr)	S (ml NTP)	Time (min)	Pressure (torr)	S (ml NTP)	Time (min)	Pressure (torr)	S (ml NTP)
1.0	165.7	7.40	1.0	167.4	7.64	1.0	165.8	6.76
3.0	163.1	7.67	2.0	165.0	7.88	2.0	164.2	6.90
4.0	162.5	7.73	3.0	163.7	8.00	3.0	163.4	6.99
5.0	162.1	7.77	5.0	162.9	8.09	4.0	163.8	7.05
6.0	161.9	7.80	7.0	162.7	8.12	5.0	162.6	7.07
7.0	161.5	7.83	8.0	162.4	8.15	7.0	162.2	7.11
10.0	161.1	7.87	9.0	162.1	8.17	8.0	161.9	7.14
12.0	168.1	8.10	10.0	161.8	8.20	9.0	161.8	7.15
14.0	167.8	8.13	11.0	164.9	8.27	10.0	161.7	7.16
16.0	167.6	8.15	12.0	164.6	8.30	14.0	168.9	7.42
20.0	167.3	8.18	14.0	164.4	8.32	16.0	168.6	7.45
25.0	167.0	8.21	16.0	164.2	8.34	20.0	168.4	7.47
30.0	166.4	8.26	25.0	163.6	8.40	25.0	167.9	7.52
40.0	166.4	8.27	30.0	163.5	8.41	30.0	167.8	7.53
50.0	166.0	8.31	40.0	163.2	8.44	40.0	167.3	7.58
80.0	164.9	8.41	50.0	163.0	8.47	60.0	166.7	7.63
100.0	164.7	8.44	60.0	162.4	8.52	72.0	166.5	7.66
120.0	164.5	8.45	80.0	162.2	8.55	100.0	165.9	7.71
160.0	164.0	8.51	90.0	162.1	8.55	120.0	165.4	7.75
200.0	163.7	8.55	120.0	161.6	8.60	150.0	164.9	7.79
250.0	163.4	8.57	180.0	161.2	8.64	180.0	164.4	7.84

RUN NO. 30			RUN NO. 61			RUN NO. 61 (contd.)		
Temp. 42.6°C			Temp. 42.6°C			Temp. 42.6°C		
Time (min)	Pressure (torr)	S (ml NTP)	Time (min)	Pressure (torr)	S (ml NTP)	Time (min)	Pressure (torr)	S (ml NTP
1.0	137.8	6.19	1.33	505.1	17.31	117.6	632.0	22.87
2.0	136.6	6.28	1.67	505.1	17.54	119.8	632.0	23.07
3.0	135.8	6.34	2.08	505.1	17.85	123.2	632.0	23.17
5.0	134.9	6.41	2.47	505.1	18.16	145.5	632.0	23.58
8.0	134.2	6.46	3.00	505.1	18.34	157.5	632.0	23.78
10.0	133.8	6.48	3.28	505.1	18.45	175.0	632.0	23.54
11.0	94.0	5.46	3.87	505.1	18.63	196.8	632.0	24.14
12.0	94.2	5.44	4.17	505.1	18.71			
13.0	94.4	5.41	4.50	505.1	18.80			
14.0	94.6	5.39	6.12	505.1	18.98			
15.0	94.7	5.38	6.42	505.1	19.03			
17.0	94.7	5.38	7.58	505.1	19.14			
20.0	94.6	5.39	10.25	505.1	19.32			
25.0	94.5	5.39	11.92	505.1	19.40			
30.0	94.4	5.40	16.08	505.1	19.56			
50.0	93.9	5.45	21.50	505.1	19.74			
80.0	93.5	5.49	32.08	505.1	19.87			
100.0	93.6	5.48	43.08	505.1	20.05			
120.0	93.3	5.51	62.33	505.1	20.18			
180.0	92.8	5.56	91.17	505.1	20.36			
1220	90.0	5.84	117.33	632.0	27.78			

RUN NO. 62			RUN NO. 62 (contd.)		
Temp. 42.6°C			Temp. 42.6°C		
Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
1.50	481.3	17.06	23.50	481.3	18.92
1.84	481.3	17.27	27.33	481.3	18.97
2.08	481.3	17.39	44.75	481.9	19.18
2.28	481.3	17.53	48.00	598.2	21.64
2.75	481.3	17.70	56.25	587.0	22.06
3.00	481.3	17.76	66.75	597.2	22.36
4.50	481.3	18.12	75.00	597.2	22.47
5.20	481.3	18.26	89.00	596.5	22.73
7.84	481.3	18.47	103.0	596.8	22.85
9.25	481.3	18.53	158.0	596.3	23.25
10.50	481.3	18.59	186.33	597.1	23.38
14.84	481.3	18.74	285.0	596.8	23.69
19.00	481.3	18.81	365.0	596.5	23.89
20.50	481.3	18.85	677.0	596.6	24.31

APPENDIX 8.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE

STEPWISE INCREASES AND DECREASES IN PRESSURE AFTER 20 HOURS.

DATA FOR FIGURE 30.

RUN NO. 22	
Temp. 42.6°C	
Pressure	S
(torr)	(ml NTP)
163.3	9.15
164.0	9.18
164.6	9.19
165.6	9.22
168.2	9.23
170.0	9.28
171.4	9.32
174.2	9.37
175.2	9.41
177.3	9.45
179.8	9.53
183.7	9.59
188.0	9.71
193.7	9.83
199.9	10.00
197.3	9.96
190.0	9.80
185.4	9.67
176.0	9.44
166.4	9.23
158.5	9.02

APPENDIX 9.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE

RATE RUNS AT CONSTANT PRESSURE AT 42.6°C ON AN EVACUATED SURFACE.

DATA FOR FIGURES 32A and 32B.

RUN NO. 40		RUN NO. 41		RUN NO. 42.	
Pressure 559 torr		Pressure 458 torr		Pressure 387 torr	
Time	S	Time	S	Time	S
(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)
1.50	18.59	2.00	16.98	2.00	14.64
2.00	18.76	4.00	17.60	3.00	15.07
3.00	-	6.00	17.91	4.00	15.37
4.00	19.82	7.00	18.07	5.00	15.43
5.00	20.02	8.00	18.02	6.00	15.60
6.00	20.16	10.00	18.20	7.00	15.77
7.00	20.30	15.00	18.27	8.00	15.77
8.00	20.38	20.00	18.47	9.00	15.83
9.00	20.46	30.00	18.65	10.00	15.92
10.00	20.58	40.00	18.72	15.00	16.09
15.00	20.70	50.00	18.75	20.00	16.23
20.00	20.93	60.00	18.76	30.00	16.34
25.00	20.97	80.00	18.93	40.00	16.38
30.00	21.02	100.00	18.99	50.00	16.51
40.00	21.13	120.00	19.14	75.00	16.61
50.00	21.37	240.00	19.32	100.00	16.76
60.00	21.47			125.00	16.83
80.00	21.51			150.00	16.86
100.00	21.61			200.00	16.98
120.00	21.69			240.00	17.02
150.00	21.87				
180.00	21.87				
210.00	21.92				
240.00	22.03				

RUN NO. 43		RUN NO. 44		RUN NO. 45	
Pressure 297 torr		Pressure 213 torr		Pressure 129 torr	
Time	S	Time	S	Time	S
(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)
3.00	12.08	2.00	9.54	2.30	6.83
4.00	12.39	3.00	9.76	3.00	6.94
6.00	12.60	4.00	9.87	4.00	7.02
8.00	12.76	5.00	10.00	5.00	7.03
10.00	12.75	6.00	10.10	6.00	7.13
15.00	13.00	8.00	10.21	8.00	7.23
20.00	13.09	10.00	10.26	10.00	7.23
30.00	13.36	15.00	10.37	15.00	7.31
40.30	13.49	20.00	10.46	20.00	7.39
50.30	13.52	30.00	10.62	30.00	7.49
75.50	13.64	40.00	10.66	40.00	7.56
100.5	13.74	51.00	10.75	60.00	7.64
150.0	13.83	53.00	10.78	80.00	7.70
240.0	14.00	75.00	10.86	100.0	7.72
		100.0	10.91	120.0	7.78
		140.0	10.97	206.0	7.85
		198.0	11.07		
		234.0	11.10		

RUN NO. 46	
Pressure 560 torr	
Time	S
(min)	(ml NTP)
2.00	17.68
3.00	18.37
4.00	18.59
5.00	18.89
6.00	18.99
7.00	19.11
8.00	19.21
10.00	19.38
12.00	19.46
15.00	19.62
20.00	19.84
25.00	19.96
30.00	20.06
40.00	20.22
50.00	20.38
75.00	20.64
100.00	20.83
126.0	20.99
165.0	21.14
200.0	21.21
240.0	21.40

RUN NO. 47		RUN NO. 47 (contd.)		RUN NO. 48		RUN NO. 48 (contd.)	
Pressure 458 torr		Pressure 458 torr		Pressure 404 torr		Pressure 404 torr	
Time	S	Time	S	Time	S	Time	S
(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)
2.17	16.47	60.00	18.51	1.25	14.33	40.00	16.64
2.50	16.64	80.00	18.63	1.50	14.58	50.00	16.73
2.75	16.80	100.0	18.74	1.78	14.62	75.00	16.83
3.00	16.92	120.0	18.79	2.17	14.97	96.00	16.95
3.25	16.98	150.0	18.84	2.60	15.12	125.0	17.06
3.50	17.08	203.0	19.02	2.89	15.16	150.0	17.11
3.75	17.10	240.0	19.07	3.18	15.18	180.0	17.21
4.00	17.15	330.0	19.22	3.57	15.41	210.0	17.24
5.00	17.31			4.00	15.51		
6.00	17.49			4.25	15.55		
7.00	17.59			4.70	15.61		
8.00	17.64			5.00	15.67		
10.00	17.77			6.00	15.74		
12.00	17.86			7.00	15.96		
15.00	17.92			8.00	16.03		
20.00	17.99			10.00	16.10		
25.00	18.18			12.00	16.16		
30.00	18.27			15.00	16.25		
40.00	18.35			20.00	16.37		
50.00	18.37			30.00	16.53		

RUN NO. 49		RUN NO. 49 (contd.)		RUN NO. 50		RUN NO. 51	
Pressure 312 torr		Pressure 312 torr		Pressure 222 torr		Pressure 321 torr	
Time	S	Time	S	Time	S	Time	S
(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)
1.17	11.83	29.50	13.83	1.05	9.04	1.17	11.25
1.43	12.03	26.00	13.89	1.38	9.19	1.67	11.59
1.67	12.14	53.00	14.02	1.67	9.36	2.00	11.71
2.00	12.31	78.00	14.10	2.00	9.36	2.50	11.87
2.50	12.53	173.0	14.33	2.67	9.64	3.25	12.13
2.75	12.59	210.0	14.40	3.40	9.78	4.00	12.24
3.00	12.71	300.0	14.53	4.33	9.90	4.35	12.33
3.25	12.72			5.73	10.03	5.50	12.45
3.50	12.83			8.95	10.17	6.67	12.56
4.00	12.85			11.48	10.31	8.58	12.69
4.50	12.95			18.88	10.47	12.75	12.88
5.00	13.06			30.00	10.60	20.00	13.05
6.17	13.18			45.00	10.74	30.00	13.22
7.00	13.20			60.00	10.80	40.00	13.28
8.00	13.29			90.00	10.93	50.00	13.41
10.00	13.40			120.0	11.04	60.00	13.53
13.25	13.50			184.0	11.15	80.00	13.67
17.58	13.62			240.0	11.23	100.0	13.71
24.00	13.74			300.0	11.30	102.0	13.76
26.00	13.78					180.0	13.94
28.00	13.82					246.0	14.03
						300.0	14.12

RUN NO. 53		RUN NO. 54		RUN NO. 54 (contd.)		RUN NO. 55	
Pressure 121 torr		Pressure 578 torr		Pressure 578 torr		Pressure 578 torr	
Time	S	Time	S	Time	S	Time	S
(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)
1.50	6.03	1.17	17.53	145.0	21.75	1.00	18.03
1.92	6.20	1.92	18.34	185.0	21.95	1.42	18.61
2.50	6.21	2.28	18.61	244.0	22.11	2.12	19.17
3.17	6.37	2.75	18.82	316.0	22.28	2.50	19.44
5.37	6.51	3.25	19.11			3.33	19.75
9.50	6.66	4.43	19.47			3.92	19.93
17.17	6.81	5.75	19.74			5.00	20.13
29.00	6.96	8.00	19.92			5.83	20.36
51.17	7.09	9.00	20.07			8.17	20.59
83.50	7.23	10.50	20.17			10.00	20.65
155.17	7.36	12.00	20.25			11.42	20.80
284.00	7.49	13.08	20.36			12.25	20.86
		14.50	20.38			14.60	20.98
		20.00	20.60			23.75	21.23
		21.00	20.60			43.00	21.44
		30.00	20.83			60.00	21.65
		40.00	20.99			80.00	21.88
		60.00	21.26			100.0	21.93
		80.00	21.44			121.0	22.07
		100.0	21.70			197.0	22.36
		120.0	21.71			300.0	22.61

RUN NO. 56		RUN NO. 58		RUN NO. 60		RUN NO. 60 (contd)	
Pressure 574 torr		Pressure 580 torr		Pressure 570 torr		Pressure 570 torr	
Time	S	Time	S	Time	S	Time	S
(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)	(min)	(ml NTP)
1.35	18.46	1.00	18.48	0.58	17.91	87.00	22.47
1.75	18.98	1.33	18.98	1.00	18.66	93.83	22.54
2.00	19.18	1.75	19.36	1.50	19.28	180.0	22.86
2.50	19.39	2.25	19.77	1.75	19.48	196.0	22.93
2.75	19.56	3.00	20.13	2.33	19.98	300.0	23.23
3.67	19.93	4.00	20.52	2.75	20.12		
5.17	20.33	5.00	20.75	3.00	20.18		
7.00	20.57	7.17	21.05	3.37	20.39		
8.00	20.71	9.00	21.17	3.92	20.59		
10.50	20.75	11.33	21.39	4.75	20.75		
12.67	21.04	20.00	21.71	5.42	20.94		
19.00	21.24	35.00	21.98	7.75	21.16		
30.00	21.44	60.00	22.24	8.92	21.27		
40.00	21.60	100.0	22.46	10.67	21.41		
60.00	21.84	155.0	22.71	12.33	21.51		
80.00	22.00	241.0	22.91	13.83	21.57		
115.0	22.22			19.25	21.72		
181.0	22.45			33.83	22.09		
304.0	22.69			43.00	22.21		
				60.17	22.41		
				64.08	22.41		

APPENDIX 10.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE

RATE RUNS AT CONSTANT FOLUME ON AN EVACUATED SURFACE.

DATA FOR FIGURES 33A and 33 B

RUN NO. 70			RUN NO. 70 (contd.)		
Temp. 42.6°C			Temp. 42.6°C		
Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
1.00	529.1	16.96	450.0	457.8	19.24
2.12	511.7	17.55	690.0	454.0	19.36
3.00	503.7	17.80	1320	448.7	19.51
4.08	497.7	17.99	2040	444.9	19.63
5.13	493.9	18.12	2820	442.0	19.70
6.25	491.7	18.19	3505	440.0	19.78
7.07	490.7	18.21	4200	437.9	19.84
8.08	489.7	18.26	5640	435.9	19.90
9.10	488.1	18.31	7200	434.0	19.96
10.17	487.5	18.32	15960	427.2	20.16
15.08	483.7	18.45			
20.18	480.8	18.53			
30.03	477.8	18.62			
40.07	475.5	18.69			
60.07	472.2	18.80			
91.08	469.1	18.89			
120.0	467.0	18.96			
150.0	465.4	19.07			
180.0	464.0	19.04			
240.0	461.9	19.11			
330.0	459.6	19.18			

RUN NO. 73			RUN NO. 73 (contd.)		
Temp. 42.6°C			Temp. 42.6°C		
Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
0.50	360.9	12.38	60.00	299.2	14.02
1.00	348.5	12.73	75.00	297.5	14.07
1.50	340.9	12.93	90.00	296.2	14.09
2.00	335.3	13.08	120.0	254.6	14.13
2.50	331.5	13.18	165.0	292.7	14.19
3.00	328.9	13.24	330.0	288.1	14.30
3.50	326.3	13.32	660.0	283.7	14.41
4.00	323.9	13.37	1155	280.0	14.49
4.50	322.5	13.42	1635	278.0	14.54
5.00	321.1	13.46	2520	275.2	14.61
6.00	318.9	13.51	3120	274.3	14.64
7.00	317.3	13.56	4320	272.9	14.67
8.00	316.9	13.57	5760	270.9	14.72
9.00	314.9	13.62	7300	269.3	14.76
10.50	313.7	13.65	8640	268.9	14.78
15.00	311.1	13.71	10080	268.3	14.80
20.00	308.6	13.77			
25.00	306.4	13.83			
30.00	304.9	13.87			
40.00	302.7	13.92			
50.00	300.9	13.97			

RUN NO. 75			RUN NO. 75 (contd.)		
Temp. 42.6°C			Temp. 42.6°C		
Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
0.50	207.0	8.48	60.00	172.0	9.24
1.00	201.2	8.61	90.00	169.0	9.31
1.50	196.6	8.71	115.0	167.5	9.33
2.00	193.8	8.77	200.0	165.0	9.39
2.50	191.4	8.82	300.0	162.7	9.64
3.00	189.6	8.86	1290	155.5	9.59
3.50	188.8	8.88	2670	152.9	9.64
4.00	187.6	8.90	4350	150.9	9.68
4.50	186.8	8.92			
5.00	186.0	8.95			
6.00	185.0	8.96			
7.00	183.4	9.00			
8.00	183.4	9.00			
9.00	182.6	9.07			
10.00	181.6	9.04			
15.00	179.2	9.09			
20.00	177.7	9.12			
25.00	176.7	9.14			
30.00	175.5	9.16			
45.00	173.1	9.21			

RUN NO. 85			RUN NO. 86			RUN NO. 87		
Temp. 25°C			Temp. 25°C			Temp. 25°C		
Time	Pressure	S	Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
1.00	391.1	21.78	1.00	343.2	20.66	1.00	258.7	17.46
2.50	365.9	22.51	2.00	323.8	21.19	2.00	243.5	17.84
3.50	356.9	22.76	3.00	313.8	21.45	3.00	235.1	18.04
5.00	348.1	23.00	4.00	307.4	21.62	4.00	230.9	18.14
7.00	344.7	23.11	5.00	303.8	21.72	5.00	228.1	18.21
8.50	342.3	23.18	6.00	301.0	21.79	6.00	226.3	18.25
10.00	340.9	23.23	7.00	299.8	21.83	7.00	224.7	18.29
15.00	337.1	23.32	8.00	298.8	21.85	8.00	223.7	18.31
20.00	335.0	23.38	10.00	296.4	21.91	10.0	222.5	18.34
25.00	333.2	23.43	15.00	293.8	21.97	15.00	219.7	18.41
30.00	331.4	23.48	20.00	292.0	22.02	20.00	218.3	18.44
40.00	335.0	23.51	30.00	285.0	22.11	30.00	216.3	18.39
50.00	328.2	23.56	50.00	286.7	22.17	50.00	213.8	18.55
73.00	325.1	23.65	100.0	283.0	22.26	100.0	210.9	18.61
100.0	323.1	23.70	156.0	280.9	22.31	150.0	209.0	18.66
150.0	320.6	23.76	210.0	279.0	22.36	200.0	207.8	18.69
200.0	318.9	23.81	1252	271.4	22.55	1285	201.9	18.82
300.0	316.4	23.87	2625	268.7	22.63	2880	198.9	18.89
1300	307.0	24.13	4310	266.0	22.69	4320	197.7	18.91
2740	302.9	24.23						
4310	298.8	24.34						

RUN NO. 88			RUN NO. 89			RUN NO. 90		
Temp. 25°C			Temp. 25°C			Temp. 25°C		
Time	Pressure	S	Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
1.00	217.3	15.21	1.00	115.3	10.46	1.00	68.1	7.54
2.00	203.9	15.52	2.00	107.9	10.61	2.00	64.1	7.60
3.00	196.9	15.67	3.00	104.5	10.67	3.00	61.9	7.65
4.00	193.1	15.77	4.00	102.5	10.71	4.00	60.3	7.68
5.00	190.5	15.82	5.00	100.7	10.75	5.00	60.3	7.68
6.00	188.5	15.87	7.00	99.1	10.78	7.00	58.5	7.71
8.00	186.5	15.91	10.00	98.3	10.79	10.00	58.1	7.72
10.00	184.9	15.95	15.00	96.3	10.84	15.00	57.1	7.73
15.00	182.9	16.00	30.00	94.3	10.87	30.00	55.8	7.75
20.00	181.1	16.03	50.00	92.4	10.92	50.00	54.5	7.78
30.00	178.9	16.08	100.0	90.3	10.95	100.0	53.2	7.81
50.00	176.8	16.13	200.0	88.2	11.00	200.0	52.0	7.83
100.0	173.3	16.20	1296	84.3	11.06	1147	49.6	7.87
200.0	170.7	16.27	2714	83.6	11.08	2695	48.4	7.89
1291	163.7	16.42	4328	83.0	11.09	4315	48.2	7.89
2472	161.2	16.47						
4320	159.7	16.50						

RUN NO. 91		
Temp. 25°C		
Time	Pressure	S
(min)	(torr)	(ml NTO)
1.00	60.1	6.94
2.00	56.7	7.00
3.00	55.5	7.02
4.00	54.3	7.04
5.00	53.1	7.07
6.00	52.7	7.08
7.00	52.7	7.08
10.00	52.3	7.08
20.00	51.1	7.10
30.00	50.3	7.12
50.00	49.8	7.13
100.0	48.4	7.15
220.0	47.4	7.17
1131	44.9	7.22
2675	44.0	7.23
4315	43.8	7.24

APPENDIX 11.

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE CHANGING FROM CONDITIONS OF CONSTANT PRESSURE TO CONDITIONS OF CONSTANT VOLUME DURING THE COURSE OF A RUN.

DATA FOR FIGURE 34.

RUN NO. 77			RUN NO. 77 (contd.)		
Temp. 25°C			Temp. 25°C		
Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
0.92	525.9	23.76	28.10	525.9	28.77
1.67	525.9	24.92	33.37	525.9	29.04
2.08	525.9	25.41	44.87	525.9	29.15
2.58	525.9	25.94	51.25	525.9	29.28
3.25	525.9	26.37	60.83	525.9	29.47
3.75	525.9	26.62	71.22	525.9	29.55
4.13	525.9	26.81	90.00	522.9	29.67
5.08	525.9	27.19	120.0	519.8	29.76
5.92	525.9	27.49	150.0	517.4	29.84
7.33	525.9	27.70	180.0	515.7	29.90
10.00	525.9	27.96	240.0	512.1	30.01
12.75	525.9	28.21	300.0	509.9	30.10
16.57	525.9	28.40	360.0	507.7	30.15
20.47	525.9	28.64	1680	491.3	30.71

RUN NO. 78			RUN NO. 78 (contd.)		
Temp. 25°C			Temp. 25°C		
Time	Pressure	S	Time	Pressure	S
(min)	(torr)	(ml NTP)	(min)	(torr)	(ml NTP)
0.92	404.5	21.78	13.63	404.5	25.68
1.50	404.5	22.69	17.65	404.5	25.82
1.92	404.5	23.31	23.75	404.5	26.00
2.67	404.5	23.73	28.25	404.5	26.10
2.92	404.5	23.97	33.78	404.5	26.20
3.33	404.5	24.21	39.82	404.5	26.30
3.55	404.5	24.41	48.38	404.5	26.40
4.47	404.5	24.64	56.48	404.5	26.55
5.17	404.5	24.76	66.63	404.5	26.62
5.63	404.5	24.95	90.00	404.1	26.71
6.00	404.5	24.99	120.0	401.1	26.79
6.37	404.5	25.08	181.0	397.1	26.91
7.37	404.5	25.22	240.0	394.7	26.98
7.95	404.5	25.28	361.0	391.4	27.07
8.75	404.5	25.36	1440	384.1	27.31
9.67	404.5	25.46			

APPENDIX 12

VINYL CHLORIDE ADSORBED ON POLYVINYL CHLORIDE CHANGING THE VOLUME OF THE SYSTEM DURING THE COURSE OF A RUN AT CONSTANT VOLUME WITHOUT ALTERATION OF THE PRESSURE

DATA FOR FIGURE 36.

RUN NO. 80.		
Temp. 25°C		
Time	Pressure	S
(min)	(torr)	(ml NTP)
1.00	522.9	24.96
2.00	504.9	26.04
3.00	495.3	26.67
4.00	490.5	26.97
5.00	485.5	27.29
6.00	483.3	27.43
7.00	482.3	27.49
9.00	479.1	27.71
10.00	478.9	27.72
15.00	475.1	27.96
20.00	473.1	28.09
30.00	470.8	28.24
45.00	467.3	28.47
70.00	464.8	28.63
80.00	463.0	28.66
100.0	461.7	28.72
120.0	459.3	28.78
180.0	456.2	28.88
300.0	450.9	29.05

LIST OF SYMBOLS USED

A = The reading recorded by the measuring arm of manometer E in figure 31.

B = The reading recorded by the measuring arm of manometer F in figure 31.

D = The dead space volume of the region on the gas burette side of stopcock X up to the 41.00 cm mark on manometer E.

F = ml of gas at N.T.P. required to exert a pressure of 10 torr in the dead space region on the adsorption vessel side of stopcock X up to the 41.00 cm mark on manometer F.

M = The volume of the manometer tubing per centimetre of length.

T_g = The temperature of the gas burette in degrees Kelvin.

T_R = Room temperature in degrees Kelvin.

V_g = Volume of gas in the gas burette.

p = Pressure in the system.

s = Amount adsorbed.

s_t = Amount adsorbed at time t.

s_∞ = Amount adsorbed at equilibrium.

APPENDIX 14

R E F E R E N C E S.

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